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These conference proceedings are comprised of presentations by conference participants dealing with the following topics: complying with applicable regulations; developing and implementing an overall waste management strategy; identifying cost-effective on-site/off-site oil waste management alternatives; minimizing liabilities; and understanding present and planned government oil waste program objectives. This document has a companion volume, Guide to Oil Waste Management Alternatives, a study of source reduction, recycling, and treatment technologies published in 1988.

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OIL WASTE MANAGEMENT
ALTERNATIVES SYMPOSIA

CONFERENCE PROCEEDINGS

Sponsored by:
California Department of Health Services

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PREFACE

The California Department of Health Services is pleased to present these Symposia Proceedings on Oil Waste Management Alternatives. These Proceedings are a compilation of the papers presented at two symposia sponsored by the Department of Health Services and the United States Environmental Protection Agency in April 1988. The Proceedings have a companion volume, Guide to Oil Waste Management Alternatives, a study of source reduction, recycling, and treatment technologies published in 1988.

The Symposia, its Proceedings, and the Guide have been produced by Energy and Environmental Research Corporation under contract with the California Department of Health Services.

Responding to the changing regulatory environment will be a challenge for firms which generate or manage oil wastes. These Proceedings and the Guide provide practical tools to assist industry in:

- Complying with applicable regulations;
- Developing and implementing an overall oil waste management strategy;
- Identifying cost-effective on-site/off-site oil waste management alternatives;
- Minimizing liabilities; and
- Understanding present and planned government oil waste program objectives.

OIL WASTE MANAGEMENT ALTERNATIVES

SYMPOSIUM AGENDA

DAY ONE: PLANNING ISSUES

Registration (7:30-10:30)

Opening Session (8:30-9:35)

- Opening Remarks:
  David Leu, CA
  Department of
  Health Services (DHS)
- Program Overview:
  Pat Nelson, EER Corporation
- CA Used Oil Picture: Tim Sparks

Regulatory Review (9:35-11:45)

- Federal Regulatory Approach:
  David Tomten, U.S. EPA

Coffee Break

- California Regulatory Approach:
  Robert McCormick, CA DHS
- Local Regulatory Approach:
  LA: Jim Wells
  Oakland: Thomas Peacock,
  Alameda County Department of
  Environmental Health
- Practical Implications:
  Peter Weiner, Heller, Ehrman,
  White & McAuliffe

Lucheon With Keynote Adress:
(11:45-1:15)

- On-site Management Overview:
  Robert Salvesen,
  RHS Associates
- Used Oil Minimization:
  David Smith, Withrow
  Lubricants Division,
  Castrol, Inc.
- Small Quantity Generators:
  Kip Prahl,
  Kip Prahl Associates

Coffee Break

- Case Study:
  LA: Bob Salvesen
  Oakland: John Rousch Naval Air
  Air Stateion-Alameda
- Oily Wastewater Pretreatment
  LA: Choong Rhee, LA County
  Sanitation Districts
  Oakland: Herbert Schott,
  Union Sanitary Dist.
- Used Oil Collection and
  Hauling: Kirk Hayward, CA
  Oil Recyclers, Inc.

Discussion (4:05-4:30)

OIL WASTE MANAGEMENT ALTERNATIVES

SYMPOSIUM AGENDA (Cont.)

DAY TWO: TECHNOLOGIES

Registration (7:30-9:00)

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  EER Corporation
- Rerefining Technology:
  Dennis Brinkman,
  National Institute for
  Petroleum and Energy Research
- Rerefining Case Study:
  John Fok, Evergreen Oil, Inc.
- Thermal Treatment:
  Michael Zimmer, Systech

Coffee Break

- PACT Process: William Copa,
  Zimpro Passavant
- Physical Treatment:
  LA: Andora Sprecher,
  Demenno-Kerdoon Oil Co. Inc.
  Oakland: Lucas Dobrzanski, Gibson
  Oil & Refining
- European Practices: Tim Sparks

Luncheon (11:50-1:10)

Emerging Technologies (1:10-3:55)

- Overview: Robert Long,
  Long Consulting, Inc.
- Supercritical Water Oxidation:
  Michael Modell
  Modell Development Corporation
- Deep Well Oxidation
  George Hartmann,
  Oxidyne Corp.
- Wet Oxidation: William Copa,
  Zimpro Passavant
- Basic Extraction Sludge
  Treatment:
  Douglas Austin,
  Resources Conservation Company

Perspective/Trends In Used Oil Management (3:55-4:20)

- Dennis Brinkman,
  National Institute for
  Petroleum and Energy Research

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Local Regulatory Approach To Oil Waste Management
Tom Peacock - Alameda County Dept. of Environmental Health

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Robert H. Salvesen - Robert H. Salvesen Associates

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Small Quantity Generators
Kip Prahl, P.E. - Kip Prahl Associates

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Recycling: The Ultimate Solution
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John R. Mullin - Fluid System Products, Inc.

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Bob Long - Long Consulting

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Wet Air Oxidation Of Oils, Oil Refinery Sludges, And Spent Drilling Muds
William M. Copa, Marvin J. Dietrich - Zimpro/Passavant Inc.

An Innovative And Demonstrated Process For Treating Hazardous Sludges And Contaminated Soils
Douglas A. Austin - Resources Conservation Co., Seattle, Washington

Perspectives/Trends In Used Oil Management
Dennis W. Brinkman - IITRI/National Institute For Petroleum & Energy Research

Biological Treatment of Wastewaters Derived from the Fuel Industry Using the Pact Process
Marvin J. Dietrich, William M. Copa - Zimpro/Passavant Inc.

An Overview of the Used Oil Picture in California - 1988
Timothy Sparks

A Review of Used Oil Policy and Practices in Countries Other Than the United States
Timothy Sparks

Dave Tomten
U. S. Environmental Protection
Agency - Washington D.C.

EPA's Evolving Used Oil Regulatory Strategy

Used oil -- a complicated problem from a regulatory perspective. It represents a valuable non-renewable resource and should be recycled when possible. It also frequently contains contaminants that can pose substantial environmental and health risks if managed improperly. This paper summarizes the U.S. Environmental Protection Agency's efforts to strike a balance between these competing concerns in its regulation development efforts.

Regulating used oil presents some special problems. Simply defining the "used oil universe" is difficult, because oil is used for so many different applications, and varies widely in chemical complexity. Each application may demand a different additive package, and introduce different contaminants through use. Approximately 1.2 billion gallons of used oil are generated each year by hundreds of thousands of generators. Approximately two-thirds is recycled, primarily for use as a fuel. The historic abuse of the used oil management system as a dumping ground for hazardous waste is another complicating factor that highlights the need for regulation of the industry.

STATUTES

Congress recognized the need to address these problems and concerns and in 1980 and 1984 enacted legislation amending the Resource Conservation and Recovery Act (RCRA) that established specific goals and provisions for regulating used oil. The Used Oil Recycling Act of 1980 (UORA) mandated the Agency to promulgate regulations establishing standards to protect public health and the environment from the risks posed by improper management of used oil. The statute also provided that "...such regulations ... not discourage the recovery or recycling of used oil."

The Hazardous and Solid Waste Amendments of 1984 (HSWA) established additional mandates and provided for additional constraints on regulation of recycled used oil consistent with Congress's earlier stated goals. These amendments establish special provisions within Subtitle C (Hazardous Waste Management) of RCRA that authorize EPA to develop a separate regulatory framework for recycled used oil regardless of whether it is listed or identified as a hazardous waste.

Congress also limited the liability of certain facilities (e.g., service stations) providing collection centers for used oil generated by do-it-yourself oil changers (DIYs) in the Superfund Amendments and Reauthorization Act of 1986 (SARA). This provision will be applicable when final facility management standards are issued.

REGULATIONS

In response to these mandates and constraints, EPA has conducted a number of studies, has promulgated regulations to restrict burning of used oil, and is developing other regulations to bring used oil under broader regulatory control.

The existing regulations (codified at 40 CFR Part 266, Subpart E) were promulgated on November 29, 1985 (50 FR 49164) and contain administrative requirements and restrictions on used oil that is burned for energy recovery. Used oil that is not burned for energy recovery is currently not regulated unless it has been mixed with a listed hazardous waste.

The rule establishes a used oil fuel specification, consisting of six parameters including four toxic metals, flashpoint, and total halogens. Used oil fuel that meets the specification is conditionally exempt from regulation, while "off-spec" used oil fuel is subject to certain restrictions and administrative requirements. The administrative requirements are minimal and place the regulatory burden on marketers and burners of off-specification used oil fuel, rather than generators and transporters. The requirements include recordkeeping and use of invoices, notifications, and required notices. Under the rule, "off-spec" used oil can only be burned in certain devices, such as industrial boilers and industrial furnaces. This rule was meant as an interim measure to reduce risks posed by unrestricted burning of used oils, until more protective controls could be developed.

Mixtures of used oil and listed hazardous waste are subject to the more stringent hazardous waste management regulations. The used oil fuel rules of 40 CFR Part 266 establish a rebuttable presumption as a means for determining when mixing of used oil and hazardous waste has occurred. Under this provision, used oil containing greater than 1000 ppm of total halogens is presumed to have been mixed with hazardous waste. The presumption can be rebutted by showing that the source of the halogens is not listed halogenated solvents.

In November of 1985, EPA also published two proposals that would bring used oil under broader regulatory control. Under one of these (50 FR 49258, November 29, 1985), the Agency proposed to list used oil as a hazardous waste under section 3001 of RCRA. Under the other (50 FR 49212, November 29, 1985), the Agency proposed management standards for recycled used oil. These proposals generated a great deal of concern within the regulated community. Public commenters overwhelmingly objected to listing used oil that was recycled as a hazardous waste, and certain facility management standards, arguing that the increased costs and stigma associated with such a blanket listing would disrupt the used oil management system, and actually be environmentally counterproductive by diverting used oil now being recycled to be disposed of in uncontrolled ways.

On November 19, 1986 (51 FR 41900), after further evaluation, the Agency published a final determination not to list used oil bound for recycling as a hazardous waste under RCRA, and set out a strategy to decide how to control used oil bound for disposal. The proposed management standards and certain other initiatives (e.g., burning controls) were deferred pending the outcome of the decision on disposal controls. Since then, the Agency has evaluated a number of options and has determined that listing for disposal only under RCRA would be preferable to use of TSCA section 6 statutory authorities to control disposal of used oil (see below).

CURRENT INITIATIVES

EPA's current strategy to minimize the potential risks posed by the improper management of used oil and encourage recycling involves using a combination of regulatory and non-regulatory programs. These initiatives are summarized below.

- EPA is developing an education program to promote the voluntary recycling of used oil from do-it-yourself oil changers (DIYs). Only 10% of DIY oil is presently recycled, as compared to 80% of industrial oil. This program will, among other things, serve as a clearinghouse for information about recycling to State and local governments, and other groups interested in recycling.

- The Agency is also planning to issue management standards to modify its existing used oil regulations and strengthen the prohibition on mixing used oil and hazardous waste. This mixing is a major contributor to total risk posed by used oil.

- EPA will place additional management controls on all used oil, including recycled used oil, through its Underground Storage Tanks program.

- After close examination, EPA has determined that used oil disposal (where used oil is unmixed with hazardous waste and does not exhibit a hazardous waste characteristic) should be controlled by a risk-based, concentration-driven listing. Recycling and disposal of used oil mixed with hazardous waste is already controlled under existing hazardous waste regulations. Disposal of used oil that exhibits a hazardous waste characteristic is also controlled under the hazardous waste rules, although recycled used oil fuel that exhibits a characteristic is exempt. However, a concentration-based listing cannot be promulgated until EPA develops a risk assessment model for oily wastes. EPA will also gather additional data on the composition of used oil for this listing.

- EPA also will propose listings for residuals from used oil recycling. These listings are also contingent on the development of the oily waste fate and transport model.

* EPA, through its Office of Toxic Substances, will act on a proposal to relax restrictions on used oil containing detectable concentrations of PCBs up to 49 ppm to allow burning in units now eligible to burn "off-spec" used oil.

Because assessing the need for a comprehensive set of management standards for recycled used oil largely depends on the outcome of the listing efforts, initiatives in the area of management standards for generators, transporters, and recyclers will be limited to those discussed above. Efforts to develop additional burning regulations are on hold this fiscal year.

LOCAL REGULATORY APPROACH TO OIL WASTE MANAGEMENT

TOM PEACOCK, Alameda County Dept. of Environmental Health

31 Mar 88

Prime responsibility for most environmental enforcement regarding oil waste rests with the State of California since oil waste is only a California waste and not an Environmental Protection Agency regulated waste. The State regulates waste from 4 section offices which makes regulation of waste generators very difficult. The North Coast section is responsible for an area from south of Monterey all the way to the Oregon border. This geographical area is really not practical to regulate small businesses out of their Emeryville office. Consequently, the Department of Health Services (DOHS) also known as the Toxic Substances Control Branch or Toxics for short has been anxious to have local agencies take over responsibility for enforcement of state laws regarding hazardous waste generators. The Toxics people sign a Memorandum of Understanding with the local agency that they will inspect and conduct enforcement activities within generators and non-permitted facilities. The local agency is usually the County Health Department although we have in our County of Alameda the City of Berkeley which has their own Health Department and also jurisdiction over hazardous waste activities.

In conducting enforcement activities the local agencies recruit and train professionals in this new field. Most come from two different areas: either as Sanitarians with sufficient chemistry training in their education, or as Chemists, Industrial Hygienists, Engineers, Geologists, or other related backgrounds. Inspections are conducted of facilities ranging from the one man shop up to very large companies which do not have facility permits from the DOHS. In recent years there has been a move to rescind ISD and permitted status so that facilities that used to come under DOHS jurisdiction are being taken over by the counties. Any company that is not sure of whether they will be inspected or which agency may have jurisdiction over them can ask their local Department of Environmental Health which is part of the County government.

In addition to the County programs which cover many but not all counties in Northern California there also are City programs. With the exception of Berkeley cities are not conducting specific hazardous waste inspections. However, a number of cities such as Hayward, Palo Alto, Sunnyvale, Fremont, Newark, Pleasanton and others have established local ordinances which may effect hazardous waste. Hayward's ordinance is very comprehensive and is called a hazardous material storage ordinance. It applies to businesses that store hazardous liquids, solids, compresses gases, radioactive materials, biologicals, and other materials. Hazardous waste in these ordinances is considered as a sub-category under hazardous material. So in addition to the State laws that a company must comply with there may also be local ordinances they must obey. Most notable are regulations limiting quantities of materials that are allowed to be on the premises and the requirement for secondary containment of materials. These are not usually required of hazardous waste generators in other jurisdictions and these storage regulations may have more impact on specific businesses than the hazardous waste laws themselves.

If these new regulations weren't enough there is another state law that is being regulated by a variety of different jurisdictions and has a severe impact on businesses that handle oil waste. The underground tank law requires permits for tanks and that includes waste oil tanks. This applies to existing tanks and may require a large expenditure of money for tank removal. It also requires double wall tanks for all new installations. The County is the prime implementer for this law but there are many cities that have chosen to issue there own permits normally through the Fire Department. Perhaps this is because about 90% of the tanks contain motor vehicle fuel or waste oil, both substances well understood by firemen. There are many examples in Northern California where the tanks are regulated by the City and the waste within them is regulated by the County, which may be difficult for the operators to understand. Most of these tank are in service station which usually have three or four tanks.

There are a number of different violations that are commonly observed regarding the proper handling, storage, and disposal of waste oil. The most common is probably the lack of proper labeling of the containers. Waste oil tanks that are underground do not require this but the common 55 gallon drum must be labeled "Waste Oil". Industry practice has been such that almost nobody has done this. It is expected that this violation will disappear as people are educated and facilities are inspected. It is a very easy one to correct. Proper containers are steel drums with tight fitting lids. Open top trash cans and drums are frequently observed which allow for contamination from rain and trash. This also is an easy violation to correct. On site disposal from spillage or intentional dumping is also all too common. In recent years haulers have been charging 10 cents per gallon or more for removal which is objectionable to many operators. They justify sloppy handling, overfilling of containers, use to keep dust down or control weeds, and even pouring down the drain with the attitude that it is only waste oil and that they have been doing it for years. These attitudes are too commonly met and it will take a great deal of education and some needed legal enforcement to get these contaminated sites cleaned up and proper waste oil handling procedures implemented. Another violation is the lack of record keeping. Waste oil used to be something that they gave away and so no record was issued or kept. This has changed and so have the laws requiring documentation of disposal. This will be easily remedied at least for those facilities that are having their waste oil legally disposed.

All Departments of Environmetal Health can render advice on waste oil handling, storage, and disposal. In most cases they can answer questions over the telephone but can also do on sight evaluation. The DOHS is also another reference agency especially their alternative technology section in Sacramento. Local agencies are in frequent contact with these other people and use them for referals or to increase their own understanding of the latest methods and technology.

I would like to be able to give each responsible individual for every jurisdiction and their phone number. This would be very difficult in this rapidly changing field and would not be very timely. The governor has put out a book "Health Effects of Toxic Substances" in 1986. It has lists of officials by jurisdiction and already many of them are wrong. Our own department just had an entire new phone system installed with all new numbers and the Hazardous Material Division is due to move to a new office next month. This is very typical. I recommend asking the appropriate County Health people for the contacts that you need. They should be able to refer you with the latest information as we do every day.

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On-Site Management Overview

by

Robert H. Salvesen, PhD, of

Robert H. Salvesen Associates

Background

On-site management of used oils means different things to different people. Management practices vary with industries; the quality and quantity, options available for treatment and disposal of used oils. For the small generator, such as a service station operator, it may merely mean keeping out cleaning solvent, water, dirt and rags. For a large, complex industry, a wide variety of oils may be handled, thereby requiring vastly different management practices. This paper and subsequent ones will attempt to cover the following:

- Descriptions of major oils used
- Minimization
- Segregation
- Waste Exchanges
- On-site contracted services
- On-site treatment
- Discharge to POTW

I will cover the first item in some detail and briefly discuss the others, but leave the major discussions to other speakers. If there are other concerns of interest, it is hoped that they will be raised during the time allowed for questions.

Major Oils Used

There are hundreds of different types of oils used for a wide variety of purposes. Some, such as engine lube oils, are formulated to satisfy a wide range of engines types and uses. Other oils may be formulated for a special application where each industry or major company may require a special additive or specific properties to suit their needs. A listing of some of the more common oil types is given in Table 1.

A brief description of some of the major types of oils follows:

- Fuels - Fuels can become used oils if they are contaminated and cannot be used for their original purpose. Fuels are also the most common means for disposal of used oils. Two major types of fuels are used, distillates and residuals. As implied,

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distillates are products which are distilled to produce specific boiling ranges for various engines such as gasoline, diesel and turbines (jets) and for clean burning fuels (domestic). Residual fuels (#4, 5, 6, bunker, etc.) may be mixtures of distilled and undistilled petroleum fractions blended to meet specific flash point, viscosity, sulfur, BTU and other properties. The heaviest residual fuels are commonly used as blending stocks for all types of used oils.

o Engine Lubricants - Gasoline engine lubes may contain from 10-30% additives and may be made from paraffinic and/or naphthenic petroleum oils. Synthetic oils are also used. Gasoline truck lubes require somewhat higher detergency than passenger cars and high viscosity index (VI) to ensure good cold-starting characteristics.

Diesel engine lubes require a relatively high level of detergency to minimize the effects of soot formation in the combustion chamber. In addition, the high compression ratio of diesel engines creates very high piston ring zone temperatures. This requires lubricants with good oxidation stability (paraffinic-base stock). Diesel lubes use high alkaline detergent additives to neutralize some of the effects of high sulfur diesel fuels.

Aviation piston engine lubes require very good oxidation stability and very high VI. Thus, lubricants for this service are paraffin-base stocks and usually contain oxidation inhibitors as well as dispersant additives.

Aircraft turbine engine lubes generally consist of di, tri and polyesters synthesized from organic acids and alcohols. These lubes are very stable, with minimal degradation due to oxidation. The used materials make excellent plasticizers and may be reclaimed for this use or blended with fuels.

o Hydraulic Fluids - Petroleum-based materials are used for many applications. These materials are similar to lube oils but generally contain a lower percentage of additives.

Synthetic fluids are employed where fire-resistance is required. These fluids consist of phosphate esters, polyglycols, polyolifins, silicones, silicate esters and halogenated hydrocarbons such as chlorofluorocarbon polymers, fluoroesters and blends of these compounds.

o Transmission Oils - Petroleum-based oils are generally used for these applications with special additives to provide shear resistance. Some synthetic oils are also used.

o Cutting and Cooling Oils - These oils may be petroleum or synthetic oil formulations. The latter are used where fire-resistance and high stability are required. Additives are used to impart special properties such as shear or high pressure resistance. Emulsifiers may also be included to enable use as a

1-2% water emulsion or to provide the ability to wash the oil after cutting operations.

o Bilge and Ballast Oils - Ships may generate large volumes of oil/water mixtures either from bilge or ballast tanks. These oils will vary considerably depending upon the fuels used and oils transported. While the concentration of oil in water may be only 0.1 to 2% by volume, the quantities generated are often so large that the separated oils can amount to very significant volumes.

o Others - The above oils make up about 80-95% of the used oils generated, but the other oils include a wide range of mainly petroleum-based materials. Some such as quench oils (oils into which hot metals are dropped for cooling), transformer, refrigerant oils, etc., may only be changed every 3-5 years or at longer intervals. In other cases such as roll oils, they may be sent out as preservatives on processed materials.

Minimization

One of the first objectives of any used oil management program is minimization of the volumes of used oils generated. Also included in this category of management is the minimization of contamination. Various ways to accomplish minimization are as follows:

o Extend the Useful Life - Listed below are ways to accomplish this objective, along with some of the related concerns.

-Increase periods between oil changes - In effect, this would require allowing the oil to get dirtier between changes. This may be acceptable, but could jeopardize engine warranties, wear or performance characteristics. It is known that some automotive engines have run over 50,000 miles between oil changes, but this is not recommended for the average user. Large industrial users can justify checking oil quality to maximize use times.

-Use a better oil - A higher quality oil may prove cost-effective. Synthetic lube oils have better wear characteristics but many engine warranties may be voided if the lubricant is not changed on a specified schedule, thus negating the advantages of synthetic lubes in some cases.

-Reduce contamination by checking seals and gaskets frequently to minimize contamination.

-Control operating conditions to avoid excessive temperatures which tend to degrade oil. Operating at extreme loads can have the same deleterious effect.

Segregation

Segregation is the key to successful reclamation and cost reduction. The most common types of contaminants that are often easy to eliminate are noted below.

- Low Flash Materials - Gasoline, carburetor cleaners, paint thinners and other volatile materials, when mixed with used oils, create severe problems in reclamation and/or disposal.

- Chlorinated or Freon Solvents - Mixing these materials with unused oils should be avoided since they severely reduce the potential for reclamation.

- Synthetic Oils and Fluids - It is often profitable to segregate these materials from used oils since the synthetic materials can be reclaimed separately. Currently, synthetics can be used as plasticizers if contamination does not exceed about 2-5%.

Waste Exchange

Waste exchange or downgrading are the same activities. Generally, waste exchange is downgrading to an off-site facility whereas downgrading is an on-site activity. Some states, areas and industries, have extensive waste exchange operations. This can be very beneficial. Examples are use of a high purity oil after drainage for another less critical application. A common use is to add an emulsifier and use the oil as a cutting or cooling oil. Some used lubes could also be used as quench oils.

On-Site Contracted Services

There are a number of companies who provide mobile units for treatment of oils. For example, steam turbine lube oils are commonly reclaimed by treatment to remove volatile hydrocarbons, water and accumulated solids. Equipment to accomplish this can be provided by outside contractors who service on-site units.

Cutting and cooling oils can also be reclaimed by similar services. These emulsified oils can degrade biologically and emit objectionable odors. Also, oils may accumulate or separate out (tramp oils) which need to be removed or reemulsified. Contracted services can provide equipment and manpower to reclaim such oils.

Outside contractors are also available to pump out accumulated used oils in drums, storage tanks, sumps, etc.

On-Site Treatment

On-site treatment for reclamation of oils should be limited to physical processing such as centrifugation, coalescense, distillation-evaporation, steam stripping and gravity settling. Suppliers of such equipment, used by numerous industries, are given in Table 2. The heart of these systems is usally a low temperature vacuum still (about 150 F) which flashes off the volatile contaminants such as fuel and water.

A description of the most common unit operations and their application to on-site reclamation is briefly discussed below. A complete system for oil reclamation may contain one or more of these units.

- Centrifugal Separators - Can be used to separate solids from used oils when settling rates need to be enhanced and gravity separators require too long a residence time and/or when space limitations require small volume equipment.

Centrifugal separators require large power requirements and are not effective when solids are trapped in emulsions.

- Coalescers - Provide large surface area media that attract one phase of an emulsion (e.g., water) and repel the oil phase. For water removal, an emulsion of used oil is pumped through the media and water droplets attached to the surface coalesce and are separated and removed. Often, filtration and coalescence are accomplished together in a combined unit called a filter-coalescer. Such units are commonly used to remove solids and water from jet fuel and other distillate fuels. Coalescers can remove water from oil down to levels of 10-5 ppm oil dependingaupon the quality of input and system design.

- Distillation Columns - Evaporators - Can improve the quality of used oils by taking advantage of differences in volatility of impurities and the material to be purified. Typically, distillation columns and evaporators can be used to remove water and highly volatile (low flash point) fuels/solvents from high flash point fuels and lubricants.

- Filters - A wide range of filters are available to separate solids from used oil streams. The nature of the filter media and design of the unit will depend on the particle size and concentration of the solids to be removed. Typical media include sand, clays and fibrous media which can also be selected to coalesce and remove water.

- Gravity Separators - These are essentially tanks of various designs which allow oil, water and solids to separate by providing sufficient residence time for separation by gravity and bouyant forces. Many gravity separators are equipped with skimmers and pumps for water and solids removal. Heaters can also be incorporated into some designs to enhance separation rates. Gravity separators are effective for oil and solids removal when the used oils to be treated are free of emulsions and when sufficient time can be provided for settling. Effluent water streams from gravity separators may contain up to 200 ppm oil and will usually require further secondary treatment to reduce oil levels so that they are safe for disposal.

Discharge to POTW

Many industries have the capabilities to discharge used oils to

POTW (generally as low concentrations in water). However, most facilities limit the total volumes accepted as well as the type and concentration of oils in the effluent. Many POTW's have limits of 50-200 ppm oil and grease in wastewaters. Permits are required and acceptable volumes may vary as a function of other demands on the POTW system.

TABLE 1

LIST OF MAJOR TYPES OF OILS USED BY INDUSTRY

Agricultural
- o Fogging
- o Pesticide Carriers
- o Spray

Automotive Lubes
- o Piston Engine
  - Diesel
  - Gas
  - Gasoline
  - Marine
- o Turbines
  - Aircraft
  - Gas
  - Steam

Bearings

Compressor

Cooling

Cutting

Electrical

Gear

Heat Transfer

Hydraulic

Industrial
- o Lubes
- o Forge
- o Form
- o Mold
- o Process
- o Quench

Ink

Metalworking

Mold
- o Ceramic
- o Glass

Oil Drilling

Pharmaceutical
- o Process
- o White Mineral

Process
- o Al Roll
- o Cu Roll
- o Steel Roll

Refrigerant

Transformer

Transmission

TABLE 2

LIST OF EQUIPMENT SUPPLIERS FOR RECLAIMING OILS*

Supplier		Equipment Capabilities Thruput G/Hr.	Equipment Costs $K	Comments
Allen Filters Inc. 417-865-2844	P. O. Box 747 Springfield,Mo.65801	N/A**	N/A	Patented trays provide thin-film evaporation. No coalescer needed. Low maintenance.
Baran & Associates Inc. 615-528-8476	P. O. Box 2997 Cookeville,Tn.38502	75-1200	N/A	Use vacuum & heat to flash off volatiles plus filters.
Gulfgate Eng. Inc. 713-644-5558	P. O. Box 262524 Houston,Tx.77207	30-3000	5-20 & up	Offer low & high vacuum systems plus filter/separator.
Pall Corp. 516-484-5400	East Hills, N.Y.	N/A	N/A	
Petrotech Division of Aquanetics Inc. 201-850-3970	P. O. Box 745 Hacketstown,N.J.07840	180 & up	13 & up	Vacuum distillation & filtration equip. used at NSY, Mare Island & Portsmouth, N. H.

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* This list is provided for illustrative purposes only and does not give all suppliers of such equipment. No endorsement or recommendation of this equipment or suppliers is to be implied.

** N/A = Information not available.

USED OIL MINIMIZATION BY IN PLANT METHODS

BY: David H. Smith

BENEFITS:

20 years ago used oil minimization was unheard of. Why? The economic payback was just not there. When oil was $0.34 per gallon and someone paid you to take it away, why bother to make an effort to minimize used oil? Consider the economics:

In 1968	$0.34	price of new oil
	- $0.10	price received for used oil
	$0.24	cost of using oil

Even if you consider 1988 dollars at 400% of 1968 dollars, you have a cost for using oil of $0.96 per gallon.

In 1988	$1.75	price of new oil
	+ $0.50	price paid for disposed of used oil
	$2.25	cost of using oil

Not only has the cost more than doubled but the generator is potentially responsible for the waste forever, a truly priceless burden to carry forward.

Clearly, there is a large economic benefit from minimizing used oil. There are ecological and social benefits as well. It has been said that in the future people will look back on us in the 20th century and wonder why we wasted all those wonderful chemical feed stocks by burning them as fuel and throwing them away in land fills.

Given the fact that we all benefit from used oil minimization, let's look at some ways to accomplish it:

Re-Use
Downgrade and Re-Use
Extend the Life
Product Selection
Outside Management

RE-USE:

Many times some simple methods will enable you to re-use your fluid. Take the example of a screw machine shop where a significant amount of oil is used. The simple draining and collection of oil from chips can be a source of oil for re-use. The oil after collection can be readied either by settling or the use of an inexpensive filter. More sophistication can be added to this process by the use of chip wringers and clarifiers, thus almost eliminating the disposal of cutting oil.

DOWN-GRADING:

In some cases a product can be deemed unfit for further service as it was originally intended and still have great value by using it in other applications. Take for instance a hydraulic fluid that leaks from a machine. In order to re-use this fluid as it was originally intended many steps would be necessary to insure the integrity of a product as sophisticated as high pressure hydraulics. We can re-use this fluid by simply understanding its physical and chemical properties, removal of gross contamination by rough filtration and the introduction of additives for re-use as a cutting oil. A good example of a similar down grading was an aerospace contractor using Mil H-5606 in test benches. The Mil Spec fluid must be discarded when the viscosity drops below a certain point. The fluid is perfectly good except for the viscosity. It would be impossible to bring this fluid back to its original state, however, by using an additive system designed for this purpose the fluid could be re-used as a straight cutting oil in the plant.

EXTENDING FLUID LIFE:

Under this heading there are several ways to minimize used oil. First, and not in any order, would be to simply have the fluid analyzed prior to changing. This method works with sumps that are fairly large and the cost of the analysis does not exceed the cost of the fluid. Some suppliers even provide this as a service to their customers.

The use of filters to extend fluid life works extremely well. There are many types of filters ranging from diatomaceous earth to deep bed. The fluid need not see the filter before being passed through the equipment. On injection molders, for example, an external bypass filter works well in keeping the fluid clean and extending fluid life.

In some cases the use of very fine filtration such as diatomaceous earth can remove additive packages. When this type of filtration is used a regular analysis of the fluid should be performed to insure proper additive levels are maintained. Again, many fluid suppliers will perform this service.

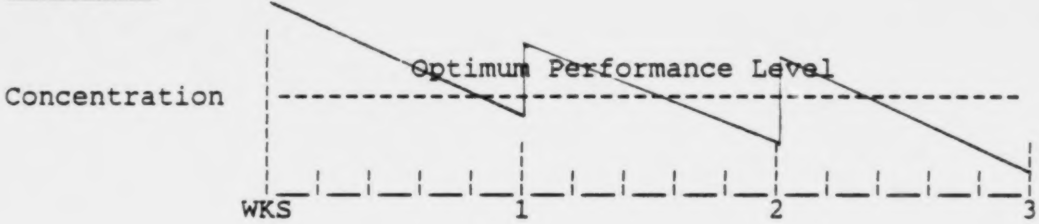
So far we have been talking primarily about straight oils used as lubricants or cutting fluids. It becomes appropriate when discussing extending life that we include water extendable oils.

These products are affected by the same things that contaminate straight oils. In addition, many things that do not affect straight oils do a great deal of damage to water extendable systems. Not only do we have dirt contamination affecting tool life and finishes, we have biological damage. This damage manifests itself in the Monday morning or rotten egg odor found after a system sets for a period of time.

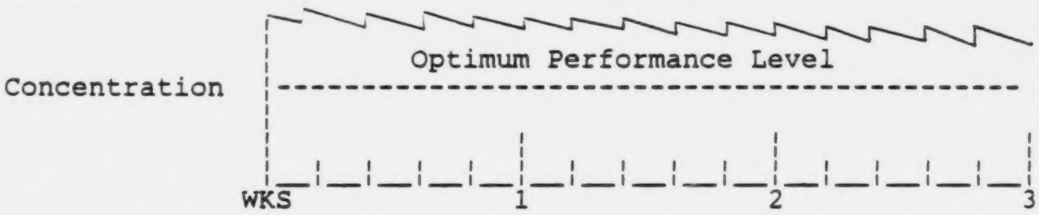
Contamination from tramp oil, such as way lubricants, and hydraulic oil from a blanket over the reservoir cutting off the oxygen supply and allowing anerobic bacteria to grow. It is this bacteria that cause the rotten egg odor. Reduction of tramp oil entering the system or skimming the oil off the surface will aid in preventing the anerobic bacteria growth. Machine operators and other employees play a large role in extending the life of these systems by keeping out things like cigarette butts, lunches and other forms of trash. It is these types of organic substances that give food for the bacteria to grow.

Concentration plays a large role in extending fluid life, also. When a system is designed to run at a concentration of 20:1 and it is allowed to lean out to 40:1 the preservative package can not keep the bacteria from growing. The frequency of addition makes a major difference also.

Example 1



Example 2



In Example 1 when we define the optimum performance level as the point at which we can begin to have system problems. You can see that with weekly additions the concentration falls below the optimum performance level and problems can occur. In addition, when the concentration is raised the system never gets back to the original level and you are heading for trouble.

In Example 2 when additions are more frequent you can see that the system stays above the optimum performance level and can be maintained there for an extended period of time.

It has been found in the management of central systems that additions of concentrate constantly by metering pumps can extend the fluid life indefinitely.

PRODUCT SELECTION:

This category can be used to extend fluid life as well as make the fluid more suitable for other methods of minimization. Extending life through product selection can take the form of more stable base oils for reduced oxidation and degradation from heat. In hydraulic applications the use of detergent dispersant packages enables filtration to be more effective by holding contamination in suspension rather than letting it deposit in the system.

Selection of products for more than one use can reduce disposal. In a screw machine application, for example, where lube oil is constantly leaking into the cutting oil, thus diluting it and reducing tool life and affecting finishes, the use of a dual purpose lube and cutting oil can reduce or eliminate the need to change the cutting oil.

In the case of water soluble products, product selection can greatly reduce disposal by moving away from conventional soluble products and toward synthetic or semi-synthetics. The exception to this is some new technology in bio stable solubles that allow utilization of the benefits of soluble oils while minimizing the drawbacks.

OUTSIDE MANAGEMENT:

The ultimate tool in minimization would be contracting with a fluid supplier to manage your fluids, thus enabling you to spend your time doing whatever it is you do best. This extension of services is logical when you consider the amount of effort put into doing whatever generates revenue for you versus the cost of non-productive tasks like managing fluids. Why not charge the fluid supplier with doing what he does best and form a partnership. This type of partnership is a true win/win situation. You win by concentrating your efforts on what you do best and leaving the management of fluids to those who do it for a living.

DHS/kd

SMALL QUANTITY GENERATORS

Kip Prahl, P.E.
Kip Prahl Associates

I. BACKGROUND INFORMATION

A. California has no formal "Small Quantity Generator" regulations

- All generators are subject to the same rules
- Small generators have special difficulty understanding what they should do

B. Most small generators in California are in the vehicle service industry (cars, trucks, tractors, equipment)

C. Used oil used to be an asset to the generator

- Good place to get rid of other wastes
    - Carburetor cleaner
    - Antifreeze
    - Paint thinner
- A small source of tax free income

D. Lots of changes in recent times:

- Now it is a costly item to have picked up
- Regulators are beginning to show up
- Storage, whether above ground or underground, is becoming a problem

E. Objectives of presentation

- Explain why these changes are occurring and what they mean to the generator
- Review some considerations in managing used oil
- Provide a few helpful hints

II. OVERVIEW OF RECENT CHANGES

A. Why have collectors begun to charge to pick up used oil

- Not a monopoly or a cartel -- lots of competitors

- Low cost of oil
- High insurance costs
- High administrative costs -- lots more paperwork

B. Where are all the regulators coming from and how should the generator protect himself

- Counties are fielding inspectors

  - You now probably pay a few
  - Off to a slow start but gaining speed

- Steps to gain compliance

  - Avoid mixing (will result in new hazardous waste streams and new disposal costs)
  - Label your containers (if above ground)
  - Retain your receipts

C. Problems with storage systems

- Underground tanks - tough rules

  - Find out if tank is leaking now, detect any future leak
  - Regulatory confusion at present

- Above ground tanks - Fire Marshalls are paying closer attention

  - Drain oil as a flammable liquid

D. Conclusion: Management should no longer overlook the mangement of this waste

- It costs money
- It carries huge risks

III. CONSIDERATIONS IN MANAGING USED OIL

A. Management options

- Have it collected and recycled
- Burn it as a heating fuel -- 90 day limit
- Recycle on site

B. Accumulating used oil - no longer cost free

- Above ground tank vs. underground tank
- The issue is risk management
- What will the Fire Marshall say

C. Hauler/Recycler considerations

- Permit status
- Insurance
- Quality of equipment/facility (most are old and ISD)
- Cost

NONE ARE RISK FREE

IV. SOME FINAL COMMENTS

A. Receipt is all you need (unless mixing occurs)

B. Get your EPA Identification Number (EPA Region IX Office: (415) 974-8860)

C. Policy of oil filters/containers

D. Get rid of old drums

E. Think cost recovery

V. WHERE TO GET HELP

- County agency (who did you pay your fees to)
- State Department of Health Services

  - Transportation Section: (916) 324-2810
  - Alternative Technology Section: (916) 324-1807

- Your hauler (maybe)

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REMOVAL OF OIL AND GREASE IN OIL PROCESSING WASTEWATERS

By

Choong Hee Rhee, Senior Engineer
Paul C. Martyn, Supervising Civil Engineer
Jay G. Kremer, Head, Industrial Waste Section
All of the Sanitation Districts of Los Angeles County

INTRODUCTION

The oil processing industry in the Sanitation Districts of Los Angeles County's (Districts) service area includes petroleum refining, used oil re-refining, petrochemical processing, crude oil and natural gas production, and related chemical companies. The volume of wastewater discharged from the oil processing industry is approximately 23 million gallons per day (MGD) which is about 35 percent of the Districts' total industrial wastewater flow and 6 percent of the 365 MGD of wastewater influent to the Districts' Joint Water Pollution Control Plant (JWPCP).

The most important pollutants in the oil processing wastewaters are conventional pollutants such as oil and grease, suspended solids and pH, and nonconventional pollutants such as phenolic compounds, COD, sulfide and ammonia. Among these pollutants, oil and grease is one of the most complicated pollutants to remove. This paper summarizes available technologies to remove oil and grease and should assist oil and grease dischargers in complying with their effluent limits.

THE COMPOSITION OF HYDROCARBON

Hydrocarbons exist in the liquid, solid or gaseous state, generally depending on the number and arrangement of the carbon atoms in their molecules. At normal temperatures and pressures, those hydrocarbon molecules with up to four carbons are gaseous, those with twenty or more carbons are solid and those in between are liquid (such as crude oils).

The simplest hydrocarbon is methane, it is comprised of one carbon atom surrounded by four hydrogen atoms. The larger hydrocarbon molecules have two or more carbon atoms joined to one another as well as to hydrogen atoms [1]. The carbon atoms may link together in a straight chain, a branched chain or a ring. The simpler hydrocarbons found in crude oils are paraffins (saturated hydrocarbon) in which each carbon atom is linked with the maximum possible number of hydrogen atoms with the generic formula of C_nH_{2n+2}. Hydrocarbons with straight or branched carbon atom chains and containing less than the maximum of hydrogen atoms per carbon atom are called "unsaturated" or "olefinic" and have the generic formula of C_nH_{2n}. Examples of these types are shown in Figure 1 [2]. Petroleum crude oils contain hundreds of different hydrocarbons, some of which are as complex as $C_{85}H_{60}$.

TEST METHODS FOR OIL AND GREASE

The test procedures used to measure oil and grease concentrations in wastewater do not determine the presence of specific substances, but groups of substances that can be extracted from a sample using a particular solvent. The sixteenth edition of *Standard Methods for the Examination of Water and Wastewater* [3] provides for the use of three test procedures to determine oil and grease concentrations in wastewater samples. These procedures include (1) the partition-gravimetric method (503A) which involves the extraction of dissolved and emulsified oil and grease using trichlorotrifluoroethane, (2) the partition-infrared method (503B) which uses an extraction process identical to the 503A method together with infrared detection methods and (3) the Soxhlet extraction method (503C) which is based on an acidification of the sample, separating the oils from the liquid by filtration and extraction using trichlorotrifluoroethane.

The above test methods have occasionally been used interchangeably under the assumption that they give comparable results. However, recent preliminary test results indicate that oils having a high concentration of water soluble naphthenic acids and oxygen-containing phenolic compounds may produce a higher oil and grease concentration using the 503A method as compared to the 503C method [4] [5].

For indirect dischargers to publicly owned treatment works subject to EPA's categorical pretreatment regulations, the final rule for the General Pretreatment Regulations, 40 CFR 403.12(b)(5)(vi), [6] states that wastewater sampling and analyses shall be performed in accordance with the techniques prescribed in 40 CFR 136 [7]. The test procedure specified for oil and grease analyses in 40 CFR 136 is the 503A method.

SOURCES OF OIL AND GREASE IN WASTEWATER

Petroleum Refining and Used Oil Re-refining

Virtually every refinery, used oil and re-refining operation, from primary distillation through final treatment, contains various fractions of oils and organosulfur compounds in their wastewaters [8]. The oil and grease in this wastewater may appear as free oil, dispersed oil, emulsified oil, soluble oil or as a coating or suspended matter.

Crude Oil Producing Facilities

Wastewater from oil field operations may contain drilling muds, brine, free and emulsified oil, tank-bottom sludge and natural gas. Many oil-bearing strata have brine-bearing formations. Oil and gas must then be separated from the wastewater; this wastewater is typically a brine waste containing some oil contamination and must be disposed.

IMPACT OF EXCESSIVE OIL AND GREASE DISCHARGES ON SEWERAGE SYSTEMS

Should there be excessive discharges of oil and grease to sewerage systems, problems may occur with the clogging of sewers and pumping plants and with the interference of biological treatment processes.

The Districts' recent studies show that the JWPCP in Carson receives approximately 390 lbs/day of benzene, 950 lbs/day of toluene and 200 lbs/day of xylene. These pollutants are occasionally associated with oil and grease discharges. Benzene is of particular concern as it has been listed as a carcinogen. These pollutants have been recently addressed in 40 CFR 60 (Standards of Performance for New Stationary Sources VOC Emissions from Petroleum Refinery Wastewater System), dated March 4, 1987. The Districts are considering developing effluent limits for benzene, toluene and xylene.

CONTROL TECHNOLOGY FOR THE REMOVAL OF OIL AND GREASE

The control technology for oil and grease removal varies in complexity, although the basic processes involve the collection and recovery of valuable oils and the removal of undesirable pollutants before discharge to a receiving system. The wastewater treatment systems operated in the oil processing wastewaters are often much larger and more complex than those found in other industries. These systems generally include gathering lines, junction boxes, collection basins and channels which transport wastewater from processing units to oil-water separators.

Oil and grease in the wastewater contained in oil processing industries can be removed by the use of widely accepted techniques. Since the removal of oil and grease depends on the condition of the oil-water mixture, the type of equipment must be carefully selected. The type of oil-water mixture may be classified as oil and grease present as free oil, dispersed oil, emulsified oil or dissolved oil. Free oil is usually characterized by an oil-water mixture with droplets greater than or equal to 150 microns [9] in size while a dispersed oil mixture has a droplet size range between 20 and 150 microns, and an emulsified oil mixture will have droplet sizes smaller than 20 microns [10]. A wastewater with an oil-water mixture where the oil is said to be soluble is a liquid where oil is not present in the form of droplets (the oil particle size would be typically less than 5 microns [11]). Figure 2 shows the classification and size range of oil droplets found in wastewaters. Soluble oils can be comprised of materials such as phenolic-type aromatic compounds which are selectively extracted to a varying degree by solvents. Extraction of these compounds was discussed in the section covering oil and grease test methods.

Theory of Gravity Oil-Water Separation

The primary function of an oil-water separator, such as the API Separator [12], is to separate free oil from wastewaters. Such gravity separators will not separate oil droplets smaller than the size of free oil nor will it break down emulsions. The three main forces acting on a discrete oil droplet are buoyancy, drag and gravity. The buoyancy of an oil droplet is proportional to its volume and the drag is proportional to the area of the droplet [13] [14]. As the diameter of an oil droplet decreases, the ratio of its volume to surface area also decreases. Because of this droplet size relationship, larger droplets tend to rise while smaller droplets tend to remain suspended. With particle diameters greater than 150 microns, the rate of rise (feet per minute) of oil droplets in wastewater may be expressed as [15]:

$$V_t = 0.0241 \left(\frac{S_w - S_o}{u} \right)$$

where;

V_t = rate of rise of oil droplet in wastewater, in feet/minute

S_w = specific gravity of wastewater at design temperature of flow

S_o = specific gravity of oil in wastewater at design temperature flow

u = absolute viscosity of the oil in wastewater at design temperature, in poises

Using the concept of the rising oil droplet as expressed above, the design of an API Separator is based on the following four relationships [9][15]:

$$A_h = F\left(\frac{Q_m}{V_t}\right)$$

$$A_c = \frac{Q_m}{V_h}$$

$$\frac{d}{B} = 0.3$$

$$L = F\left(\frac{V_h}{V_t}\right)d$$

where;

A_h = a minimum horizontal area, in feet^2

F = design factor for turbulence and short-circuiting factor (API design manual)

Q_m = wastewater flow, in feet^3/minute

A_c = a minimum vertical cross-sectional area in feet^2

V_h = horizontal flow velocity, in feet/minute, not to exceed 15 V_t or 3 feet/minute

d = depth of wastewater, in feet

B = width of separator chamber, in feet

L = length of separator chamber, in feet

When a free oil or dispersed oily water mixture is brought to a relatively quiescent state and given sufficient time, the oil droplets will coalesce and eventually separate from wastewater, forming a continuous floating oil layer which may be skimmed off. In designing a gravity separator, Beychok [15] augmented the API manual on certain points by giving an example of an API design. Figure 3 [16] shows the effect of detention time on oil removal by gravity separation. This figure shows that a drastic reduction of oil (approximately 70 percent) can be achieved within 40 minutes and that no appreciable improvement of oil removal can be seen after two hours of detention time.

Dissolved Air Flotation Oil-Water Separation

Dissolved air flotation (DAF) devices utilize the gravity separation concept for the removal of oil and grease from wastewater but tend to be more effective than API Separators in removing the dispersed oil mixture because the buoyancy differential is enhanced by induced small air bubbles. Coagulant aids such as polyelectrolytes are commonly used to promote agglomeration of the oil-bearing matter into large flocs which are more easily removed [17]. The DAF device is reported effective in producing an effluent with 1 to 20 mg/l of oil and grease [18].

Figures 4 and 5 [19] show oversimplified schematics of DAF devices with and without a recycling system. In Figure 4, the entire waste stream is saturated with air under pressure, followed by the subsequent release of the pressure and bubble formation at the inlet to the flotation chamber. This scheme creates a maximum gas solution at any particular pressure, thereby achieving maximum bubble contact with the oil.

In Figure 5, the recycling operation consists of pressuring and dissolving air in a recycle stream of clarified effluent. The pressure is released when the bubble-containing recycling stream is mixed with the untreated wastewater influent flow. A DAF device with a recycling system does not disintegrate the formed floc by the shearing action of the pressure pump. However, the recycling system requires a large flotation chamber.

The DAF device is, in general, commonly used in refineries to enhance oil and suspended solids removal. Some of the refineries in the Districts' service area are increasing the number of DAF devices to achieve the Districts' imposed oil and grease limit of 75 mg/l.

The use of chemical coagulants, such as alum or iron salts, has been an integral part of the DAF process where emulsion breaking is necessary. These chemicals function by modifying the liquid/liquid and liquid/air surface properties. For instance, those coagulants serve to decrease the interfacial tension between the dispersed oil phase and the wastewater and increase the interfacial tension between the air bubbler and the oil phase. Consequently, these chemicals and physical phenomena tend to increase air bubble-oil droplet adhesion. Enhancing this adhesion may also involve acidification and demulsification. With a properly operating DAF unit, refineries can remove oil and grease globules greater than 40 microns [10]. These coagulants generally react as follows [20]:

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4$$

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

Figures 6 and 7 [21] show the effects of coagulant chemicals on oil and grease removal. These figures indicate that the best result can be obtained at pH 8.5. In this particular case, the initial concentration of oil and grease was 200 mg/l. Almost 100 percent of the oil and grease was removed at the alum dosage of 100 mg/l while almost 100 percent of the oil and grease was removed at 50 mg/l of dosage of ferric sulfate. It is also noted that more than 85 percent of the oil and grease was removed with only 10 mg/l of ferric sulfate at pH 8.5. As seen, pH is a major control parameter for coagulation and higher dosage of coagulant is not necessarily effective in oil and grease removal.

Induced Air Flotation Oil-Water Separation

The WEMCO unit, or WEMCO Depulator, is an example of an Induced Air Flotation (IAF) device which is often used by crude oil producers and some petroleum refineries. Figure 8 [22] shows the cross section of an IAF unit. The principle of the IAF is that an intimate mixture of air and mineral-laden liquid is forced through nozzles which provide the separating action necessary to create millions of bubbles. The bubbles are then disseminated throughout the flotation chamber. Oil and suspended solids attached to the air bubbles are carried to the surface of the water where they form a froth. A skimmer paddle sweeps the oil and solids-laden froth into an overflow chamber. Some units use nitrogen gas or natural gas drawn with crude oil instead of induction of air in order to exclude oxygen from the WEMCO unit. Mittelhauser Corporation in Berkeley, California reported that IAF and DAF units following a properly designed API separator can achieve 95 and 98 percent oil and grease removal, respectively.

Ultrafiltration Removal of Oil and Grease

Carbon adsorption or membrane filtration using reserve osmosis treatment is very effective to remove dissolved and emulsified oils [23]. The concept of ultrafiltration is based on the sieving action of a membrane retaining molecules larger than the membrane pores. Reverse osmosis uses a semipermeable membrane to filter dissolved matter using very high pressures; an extremely high quality feed is required for the efficient operation of reverse osmosis facilities. The effluent from these operations contains essentially no oil and grease. However due to the large capital and operating costs associated with these devices, they are utilized very infrequently. In the Districts' service area only one refinery has such a treatment facility (carbon adsorption) and this process is used only to treat lightly contaminated rainwater runoff when it cannot be accommodated by other treatment procedures.

Biological Treatment

Biological treatment is generally effective in degrading dissolved oils and other types of stabilized emulsions which cannot be destabilized by chemical coagulants. However, a biological system is only effective on highly dilute oil-contaminated wastewaters because mineral-based oils are adsorbed by the microorganisms faster than they can be metabolized. In activated sludge systems, the adsorbed oil tends to damage sludge settling characteristics and cause system failure [20]. It has been reported that biological organisms are efficient in oxidizing dispersed or emulsified oil, but large amounts of free oil (in excess of approximately 0.1 lb/lb MLSVSS) must be avoided [24] [25].

At present, the oil processing industries in the Districts' service area have not found it necessary to install biological treatment systems to meet the discharge limit of 75 mg/l limit of oil and grease. Biologically treated effluent typically contains less than 10 mg/l of oil and grease [26].

CONSEQUENCES OF ILLEGAL DISCHARGES OF OILY WASTES

The Districts' oil and grease discharge limit for oil processing operations is 75 mg/l, based on the 503A analysis method. The EPA pretreatment regulations for the petroleum refining category provide for an oil and grease discharge limit of 100 mg/l.

The Districts monitor industrial wastewater dischargers through three separate mechanisms. The Districts employ Industrial Waste Inspectors who conduct on-site inspections to confirm compliance with the Districts' Wastewater Ordinance and permit conditions. Inspectors frequently collect grab samples in conjunction with these inspections. Composite samples are collected by the Districts' Monitoring Crews. These samples usually consist of several discrete aliquots taken over a 24-hour period. In addition, many industrial dischargers are required to monitor their own wastewater and report these results to the Districts.

The Districts' enforcement program consists of several administrative procedures. These include: (1) Warning Notice, (2) Notice of Violation, (3) Final Notice of Violation and (4) District Attorney Conference and potential court action. The Districts may also suspend an Industrial wastewater Discharge Permit when such a suspension is necessary to stop a discharge which presents an impending hazard to the local environment or to the Districts' sewerage system.

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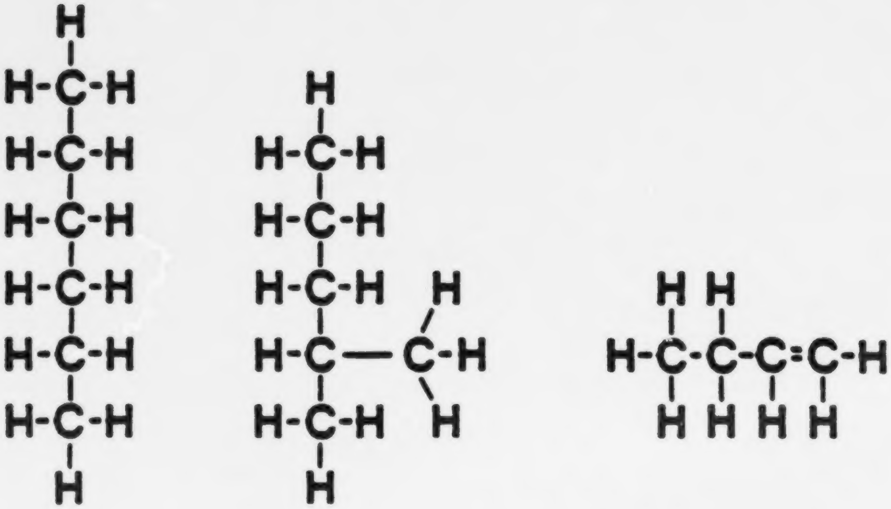

n-HEXANE i-HEXANE BUTYLENE

SATURATED, C_nH_{2n+2} UNSATURATED, C_nH_{2n}

FIGURE 1 / EXAMPLE OF SATURATED AND UNSATURATED HYDROCARBON

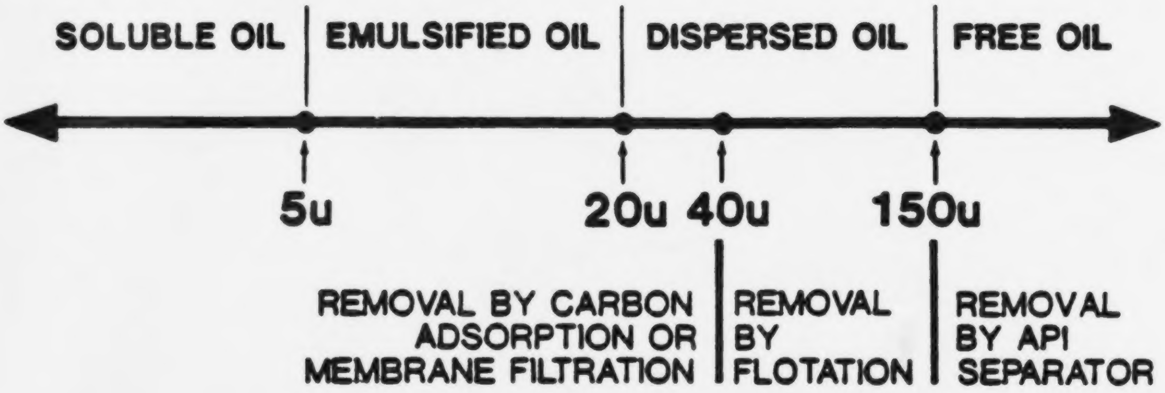
SOLUBLE OIL
EMULSIFIED OIL
DISPERSED OIL
FREE OIL
5u
20u
40u
150u
REMOVAL BY CARBON ADSORPTION OR MEMBRANE FILTRATION
REMOVAL BY FLOTATION
REMOVAL BY API SEPARATOR

FIGURE 2 / CLASSIFICATION AND SIZE RANGE OF OIL DROPLETS

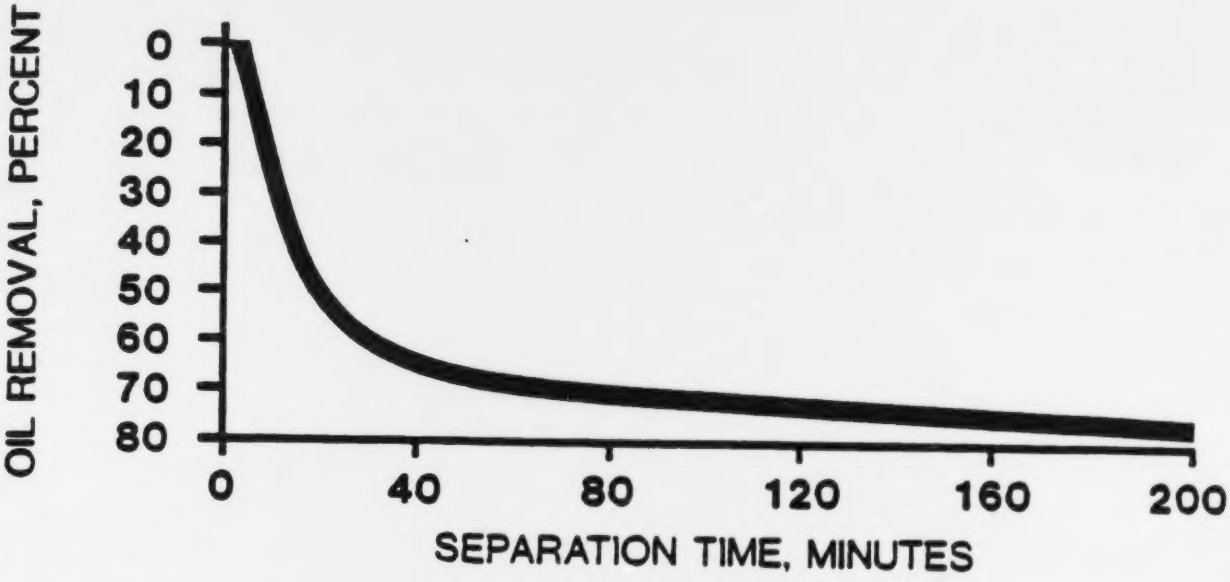

FIGURE 3 / EFFECT OF DETENTION TIME ON OIL REMOVAL BY GRAVITY SEPARATION

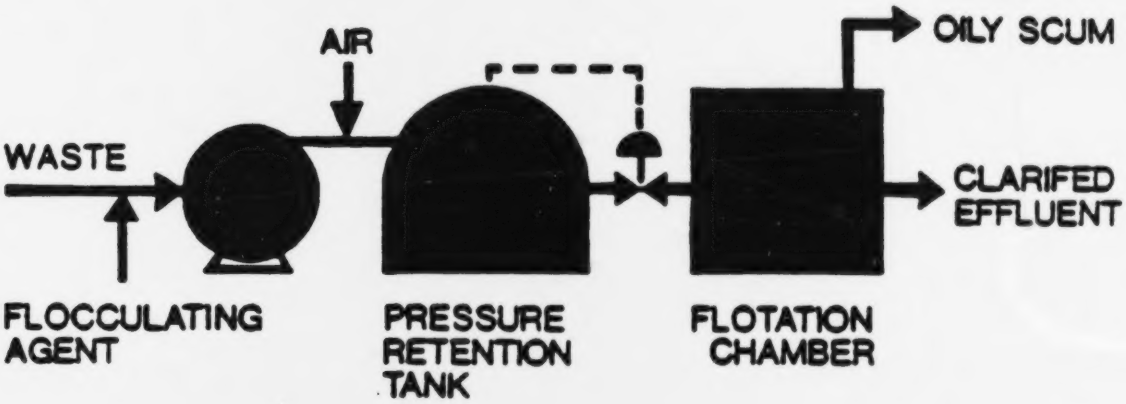
AIR
OILY SCUM
WASTE
CLARIFED EFFLUENT
FLOCCULATING AGENT
PRESSURE RETENTION TANK
FLOTATION CHAMBER

FIGURE 4 / SCHEMATIC OF DISSOLVED AIR FLOTATION WITHOUT RECYCLE SCHEMATIC

34

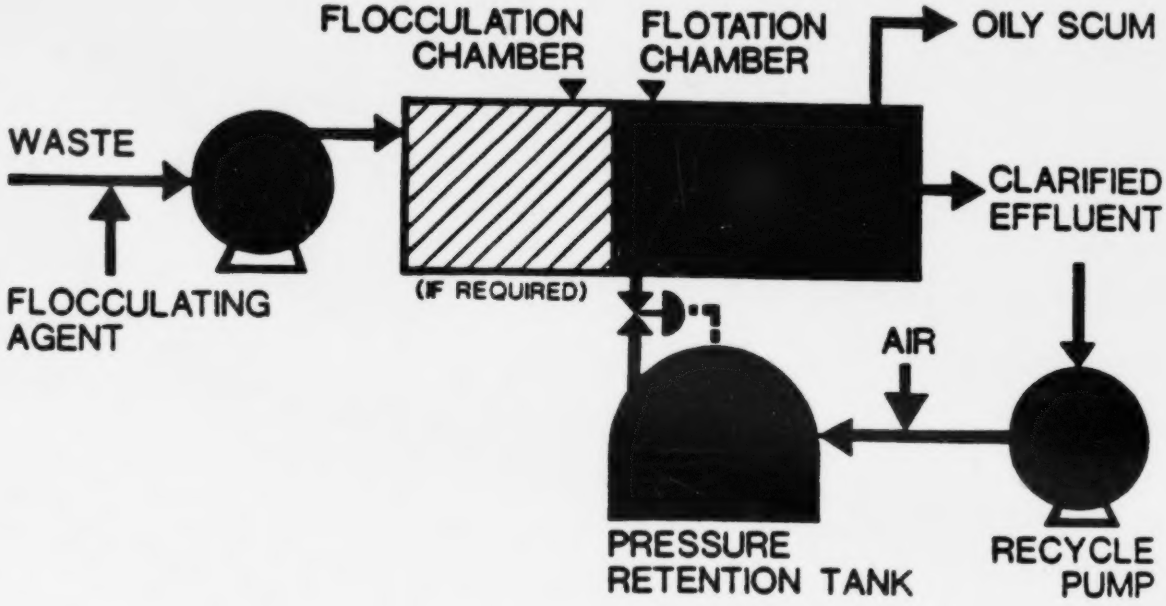
FLOCCULATION CHAMBER
FLOTATION CHAMBER
OILY SCUM
WASTE
CLARIFIED EFFLUENT
FLOCCULATING AGENT
(IF REQUIRED)
AIR
PRESSURE RETENTION TANK
RECYCLE PUMP

FIGURE 5 / SCHEMATIC OF DISSOLVED AIR FLOTATION WITH RECYCLE

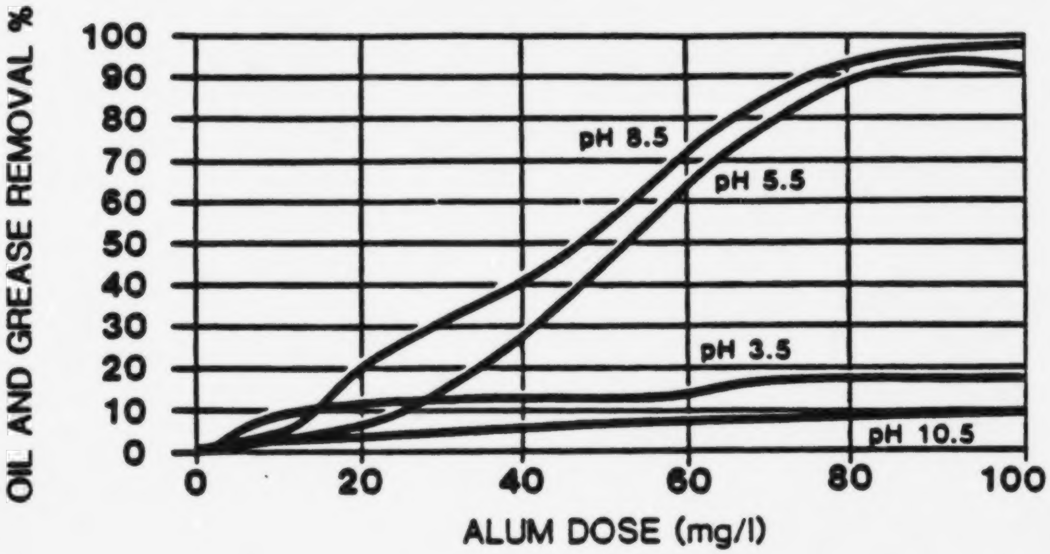

FIGURE 6 / OIL AND GREASE REDUCTION WITH $Al_2(SO_4)_3$

35

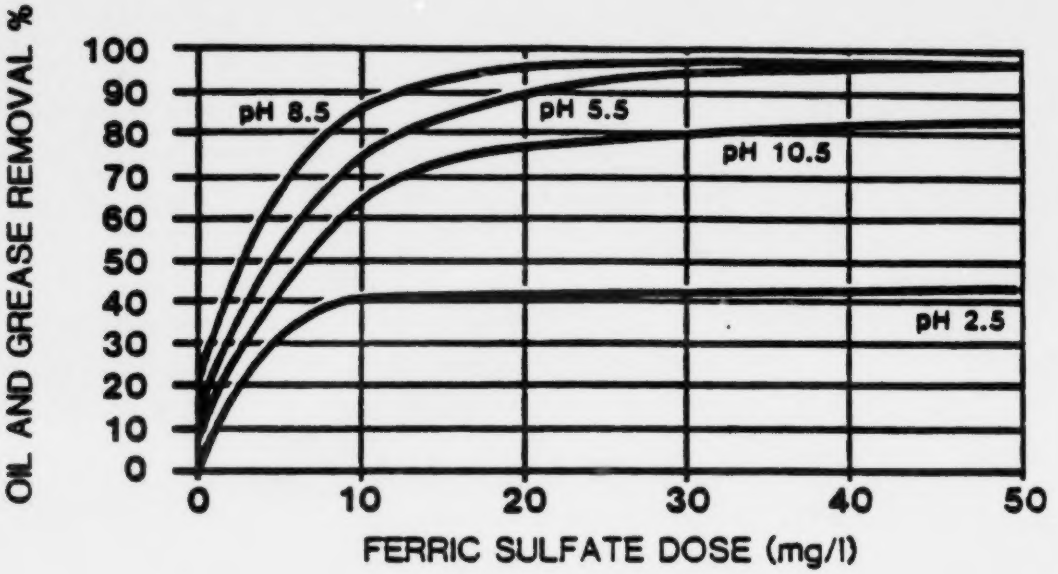

FIGURE 7 / OIL AND GREASE REDUCTION WITH $Fe_2(SO_4)_3$

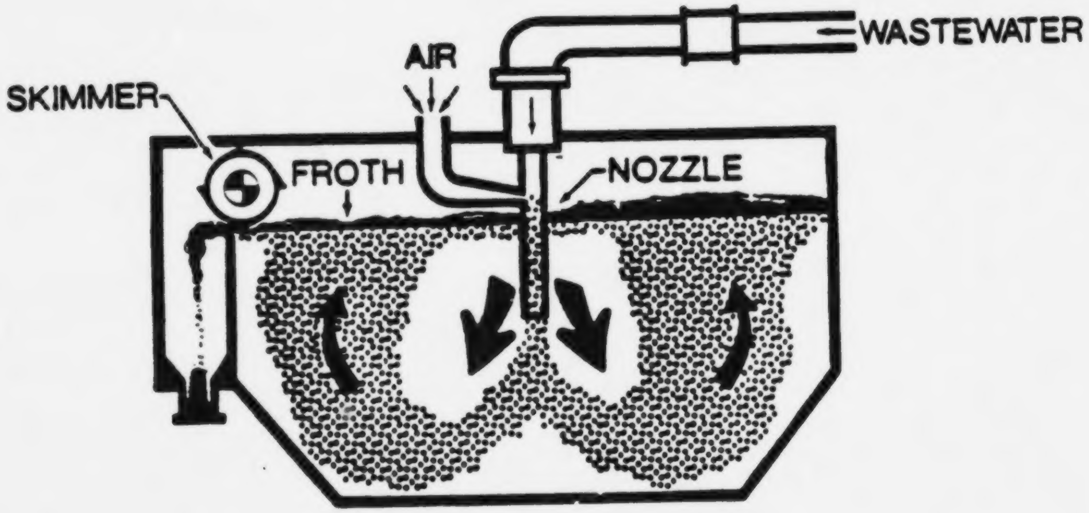
WASTEWATER
AIR
SKIMMER
FROTH
NOZZLE

FIGURE 8 / CROSS SECTION OF INDUCED AIR FLOTATION UNIT

Dr. Herbert Schott
Union Sanitary District

THE DISCHARGE OF OILY WASTEWATER TO TREATMENT PLANTS

The discharge of wastewaters containing fats, oils and greases (FOG's) to the sewer system is regulated by most treatment plants. In setting discharge limits for these types of materials, a distinction is generally made between those materials of biological origin (animal fats, vegetable oils, etc.), which generally result from the processing of foods, and those of a mineral origin (hydrocarbon solvents, gasoline, lube oils, paraffins, etc.), which generally result from industrial manufacturing processes. Since the biodegradability of the hydrocarbon type wastes from industrial sources, service stations and vehicle wash areas, is less than that for the material resulting from food processing operations, the limits set by agencies are usually more stringent for the hydrocarbon or petroleum derived material. For example, the limits set by the Union Sanitary District in Fremont, which are typical of those around the San Francisto Bay Area, allow the discharge of 300 mg/l of FOG's from biological sources, while the hydrocarbon FOG's are regulated to a 100 mg/l limit.

The testing for the oil and grease content of a wastewater is usually performed using either freon or hexane as an extracting solvent in accordance with EPA approved procedures. Absorption on a silica gel column of the more polar biological FOG's is generally used to determine the percent of the hydrocarbon fraction of the extracted fats, oil and greases in the wastewater sample.

The control of FOG's of biological origin, which is important due to the large number of sources (primarily restaurants) present in a service area, and the impact the material has on collection system maintenance, is a whole subject by itself, and the rest of this discussion will concentrate on dealing with petroleum based oils.

The presence of oily wastes in wastewater can be in several forms. The material can either be in a free, emulsified or dissolved state. Of the three forms, the treatment to remove either emulsified or dissolved oil is generally more complex and expensive. In many instances, chemicals, such as detergents or other solubilizing agents, have been added to induce the oil to remain in the emulsified form and drastic steps must be taken to break the emulsion before the oil can successfully be removed.

Pretreatment for the removal of free floating oil in wastewater streams is usually accomplished by taking advantage of the specific gravity difference between the organic material and water. The waste stream or wastewater batch is discharged into a separator unit where the water and oil have a chance to separate and the oil is given an opportunity to float to the surface. Removal of the floating oil is then accomplished through either skimming or allowing it to drain into a waste oil holding tank.

The most frequently used type of separator is the API (American Petroleum Institute) type, which can remove up to 60 to 99% of the free oil in a waste stream.

THE DISCHARGE OF OILY WASTEWATER TO TREATMENT PLANTS

The efficiency of a separator unit is dependent upon several factors, including the specific gravity difference between the oily material and water, the temperature of the waste stream, the globule size of the oil droplets in the wastewater and the retention time in the separator. Of these various parameters, the control of the wastewater retention time in the separator is often the easiest variable to control. The effective retention time can be increased by simply increasing the size of the separator, or more often, by installing a series of parallel plates within the separator through which the wastewater flows. These parallel or corrugated plate units provide additional surface area with which the flowing water makes contact and which allows further separation to occur.

When emulsified oils are present, gravity separation or primary treatment is not sufficient to treat the wastewater to meet acceptable standards, and secondary treatment, or emulsion breaking, is required. Emulsions can be broken by a variety of means, including the changing of the pH and the temperature of the wastewater, and through the addition of chemicals such as polyelectrolyte coagulants or flocculents such as alum or lime. In rare instances, chemical demulgaters may need to be added to assure adequate treatment.

Once the emulsion is broken, the resulting free oil is most often removed through the use of a dissolved air flotation (DAF) unit. In the unit, dissolved air held under pressure is suddenly released, and the resulting fine bubbles carry the oil globules and fine solids to the surface, where they may be removed through skimming or draining. This type of pretreatment, which will generally remove 90 to 95% of the incoming oil load, is often used after most of the initially present free oil has been removed by an API type separator.

In many instances, depending on the source of the wastewater, trace contaminants such as heavy metals or toxic organics are present as part of the oily wastewater stream, and pretreatment of the stream to remove the oil allows the discharge to also meet heavy metal limits similar to those of the District which are listed below:

0.1 mg/l arsenic
0.2 mg/l cadmium
2.0 mg/l copper
1.0 mg/l cyanide
1.0 mg/l lead
0.01 mg/l mercury
1.0 mg/l nickel
0.2 mg/l silver
0.5 mg/l total chromium
3.0 mg/l zinc

The discharge of oily wastewater or waste oil in excess of ordinance limits is strictly prohibited due to the detrimental effect this action can have upon the treatment plant and collection system operations of an agency. In the collection system, the discharge of oils and solvents presents both a health hazard to the work crews maintaining the system, as well as being a fire or explosion hazard. Oil and greases also have a tendency to intermix with the normal solids and debris found in wastewater to form a cake type material which causes blockages in the lines and significantly increases the cost of maintaining the conveyance system.

If free floating oil or solvents reach a pump station or a treatment plant, they can pool and cause a fire or explosion hazard at these facilities. Additionally, free floating oil will coat monitoring probes and other equipment with a sticky scum layer which is very difficult to remove. In the aeration basins, which are the main component of most secondary biological treatment systems, free oil and oil scums will cause both a filthy grey froth to form on top of the liquid, as well as interfere in the treatment process by coating the biological floc. The coating of the floc drastically reduces the efficiency of the oxygen transfer process necessary for effective treatment.

Since oily wastes are not readily biodegradeable, they usually receive insufficient treatment and pass through the treatment plant untreated into the receiving water where they have a negative impact on the receiving water quality. In addition to this "pass through" aspect, the material usually exhibits also an inhibitory influence on the treatment process itself (besides the oxygen transfer interference) due to the presence of toxic compounds (both organic and inorganic) found in this type of wastewater. These toxic compounds are harmful to the biological system and will cause the treatment of all incoming wastewater to decrease until the system has a chance to recover. Thus, the overall discharge quality from a treatment plant will suffer not only from the oil pass-through, but also from the overall inhibitory effect.

Since the impact of unauthorized oil waste discharges to a treatment plant can be quite severe, anyone guilty of allowing such discharges to occur may be subject to strict penalties. In general, the consequences of illegally discharging any unacceptable material to the sewer system can range from a simple "Notice of Violation" to monetary fines and possible criminal charges. Since waste oil has been classified as a hazardous material in California, the deliberate or persistent discharge of this type of material by itself or in excess of allowable limits would subject the discharger to not only local enforcement action by the treatment plant, but also to referral to the District Attorney's office for full criminal prosecution.

CALIFORNIA OIL RECYCLERS INC.

Used Oil Collection and Hauling

by Kirk Hayward

A. Collection variables.

1. Volumes of used oil generated
2. Size and numbers of collectors.
3. Size and locations of reprocessing/rerefining facilities.

B. Considerations for selecting a used oil hauler.

1. Permits and licenses.
2. Insurance coverage of the hauler.
3. Facility which your waste will be treated, recycled and/or disposed of, and their permits, licenses, and insurance. Ultimate disposition of waste: recycled, rendered nonhazardous, landfilled.
4. Professionalism that hauler displays.
5. Training given to the haulers employees.
6. Services offered.
7. Knowledge and compliance of pertinent laws.

C. Manifesting

1. Uniform Hazardous Waste Manifest
    - a. Who must use it.
    - b. Proper completion
    - c. Responsibilities for completion
2. Modified manifesting system for used oils.
    - a. Rules for using the modified manifest system.
    - b. Who can use this system.
    - c. Receipts necessary for proper completion.
    - d. Responsibilities for completion.

D. Generator Liabilities

- a. Liabilities for generation, transportation and disposal/recycling.

6880 SMITH AVENUE NEWARK, CA 94560 (415) 795-4400 (800) 972-5284 FAX: (415) 791-0126

A MEMBER OF THE EVERGREEN GROUP OF COMPANIES DEDICATED TO THE PROTECTION OF THE ENVIRONMENT

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CALIFORNIA OIL RECYCLERS INC.

6880 SMITH AVENUE • NEWARK, CALIFORNIA 94560
(800) 972-5284 • (800) THE OILS
EPA NO. CAD 980 695761

A Member of the Evergreen Group of Companies
Dedicated to the Protection of the Environment

INVOICE NO. 104151

MANIFEST # ____________________

____________________ DATE ____________ 19____

____________________ PHONE ____________________

____________ ZIP ________ CUST # ____________________

MATERIAL	GALS/BBLS/ETC.	PRICE	AMOUNT
WASTE OILS COMBUSTIBLE LIQUID NA1270			
TSDF: EVERGREEN OIL INC.			
		TOTAL	

6880 SMITH AVE.
NEWARK, CA 94560 CAD 980887418

PAYMENT DUE IN 7 DAYS

I CERTIFY THAT THE AMOUNTS SHOWN ABOVE TO BE CORRECT AND THAT, UNLESS OTHERWISE NOTED, THE MATERIAL IS USED OIL. I ALSO CERTIFY THAT I HAVE READ THE CONDITIONS AND INDEMNIFICATIONS ON THE REVERSE SIDE OF THIS FORM AND I UNDERSTAND AND ACCEPT THEM

SIGNATURE OF DRIVER: ____________________

____
SIGNATURE OF GENERATOR

State of California—Health and Welfare Agency
Form Approved OMB No. 2050—0039 (Expires 9-30-88)
Please print or type. *(Form designed for use on elite (12-pitch typewriter).*

Department of Health Services
Toxic Substances Control Division
Sacramento, California

UNIFORM HAZARDOUS WASTE MANIFEST

1. Generator's US EPA ID No. C A D 9 8 0 6 9 5 7 6 1
Manifest Document No.
2. Page 1 of 1
Information in the shaded areas is not required by Federal law.

3. Generator's Name and Mailing Address
CALIFORNIA OIL RECYCLERS, INC.
6880 Smith Avenue, Newark, CA 94560

4. Generator's Phone (415) 795-4410

A. State Manifest Document Number 87537217
B. State Generator's ID H A H 0 3 6 - 0 1 4 4 9 4

5. Transporter 1 Company Name CALIFORNIA OIL RECYCLERS, INC.
6. US EPA ID Number C A D 9 8 0 6 9 5 7 6 1
C. State Transporter's ID
D. Transporter's Phone (800) 972-5284

7. Transporter 2 Company Name
8. US EPA ID Number
E. State Transporter's ID
F. Transporter's Phone

9. Designated Facility Name and Site Address
EVERGREEN OIL, INC.
6880 Smith Avenue
Newark, CA 94560

10. US EPA ID Number C A D 9 8 0 8 8 7 4 1 8
G. State Facility's ID ~~C A D 9 8 0 8 8 7 4 1 8~~
H. Facility's Phone (415) 795-4400

11. US DOT Description (Including Proper Shipping Name, Hazard Class, and ID Number)	12. Containers No.	12. Containers Type	13. Total Quantity	14. Unit Wt/Vol	I. Waste No.
a. WASTE PETROLEUM OILS, NOS, COMBUSTIBLE LIQUID, NA 1270	001	TT		G	State 221 EPA/Other
b.					State EPA/Other
c.					State EPA/Other
d.					State EPA/Other

J. Additional Descriptions for Materials Listed Above
1.1 - Waste Oils
1.2 - Water

K. Handling Codes for Wastes Listed Above
a.
b.
c.
d.

15. Special Handling Instructions and Additional Information

WEAR RUBBER GLOVES

16. **GENERATOR'S CERTIFICATION:** I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked, and labeled, and are in all respects in proper condition for transport by highway according to applicable international and national government regulations.

If I am a large quantity generator, I certify that I have a program in place to reduce the volume and toxicity of waste generated to the degree I have determined to be economically practicable and that I have selected the practicable method of treatment, storage, or disposal currently available to me which minimizes the present and future threat to human health and the environment; OR, if I am a small quantity generator, I have made a good faith effort to minimize my waste generation and select the best waste management method that is available to me and that I can afford.

Printed/Typed Name
Signature
Month Day Year

GENERATOR

17. Transporter 1 Acknowledgement of Receipt of Materials
Printed/Typed Name
Signature
Month Day Year

18. Transporter 2 Acknowledgement of Receipt of Materials
Printed/Typed Name
Signature
Month Day Year

TRANSPORTER

19. Discrepancy Indication Space

20. Facility Owner or Operator Certification of receipt of hazardous materials covered by this manifest except as noted in Item 19.
Printed/Typed Name
Signature
Month Day Year

FACILITY

DHS 8022 A (1/87)
EPA 8700—22
(Rev. 9-86) Previous editions are obsolete.

White: TSDF SENDS THIS COPY TO DOHS WITHIN 30 DAYS
To: P.O. Box 3000, Sacramento, CA 95812

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TREATMENT OF OIL WASTE

By Peter Maly, EER Corp.

1.0 Introduction

The goal of this section is to define existing treatment technologies that are used to recycle, rerefine, destroy, and recover energy from oil waste. This goal will be achieved by a series of papers by authors with industrial experience in oil waste treatment techniques. Specifically, the discussions will summarize:

- o Technological concepts
- o Applicability to oil waste steams
- o Extent of use
- o Advantages and disadvantages
- o Product streams

Oil waste treatment is performed extensively. Currently in the U.S., 1.2 billion gallons of used oil per year is generated, and 0.8 billion gallons enters treatment plants. In California, 130 millions gallons per year is generated, and 50 million gallons enters treatment plants. In California, after oil waste has been treated, 80 percent is used as fuel oil, 9 percent as asphalt, 5 percent as lube oil, and 6 percent as other products.

2.0 Classification of Treatment Technologies

Figure 1 is a decision tree illustrating the applicability of treatment options. Treatment technologies can be divided into processes designed to reutilize the oil, and processes designed to reduce the volume and hazard of the waste. Figure 2 summarizes the different treatment technique categories.

2.1 Material Reutilization

The first treatment category consists of material reutilization processes. Reutilization processes recover the oil found in oil waste, allowing it to be used again. These processes include reuse and recycling. Reuse

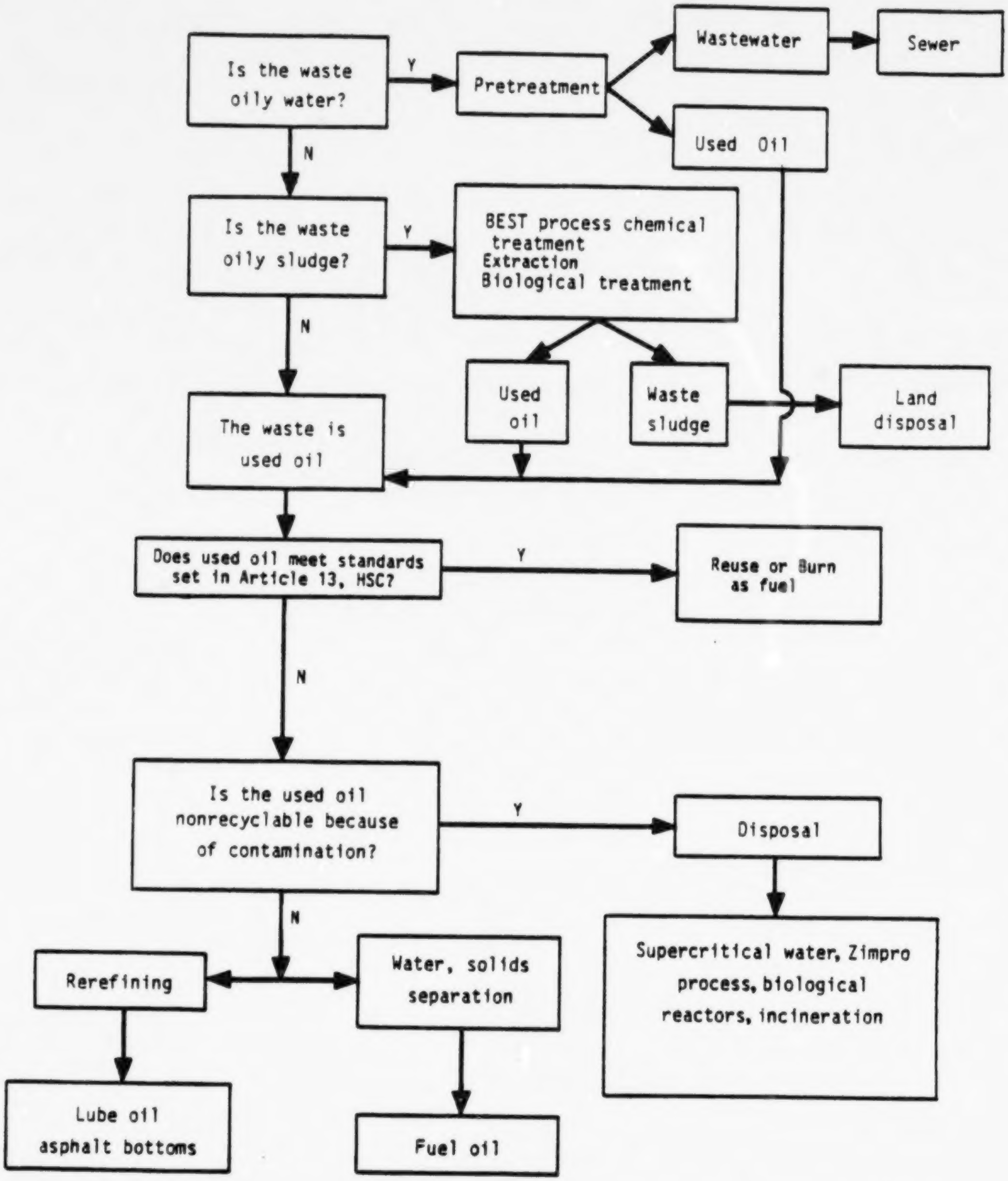
Is the waste oily water?
Y
Pretreatment
Wastewater
Sewer
Used Oil
N
Is the waste oily sludge?
Y
BEST process chemical treatment
Extraction
Biological treatment
N
Used oil
Waste sludge
Land disposal
The waste is used oil
Does used oil meet standards set in Article 13, HSC?
Y
Reuse or Burn as fuel
N
Is the used oil nonrecyclable because of contamination?
Y
Disposal
N
Rerefining
Water, solids separation
Supercritical water, Zimpro process, biological reactors, incineration
Lube oil asphalt bottoms
Fuel oil

Figure 1. A decision tree illustrating used oil management options.

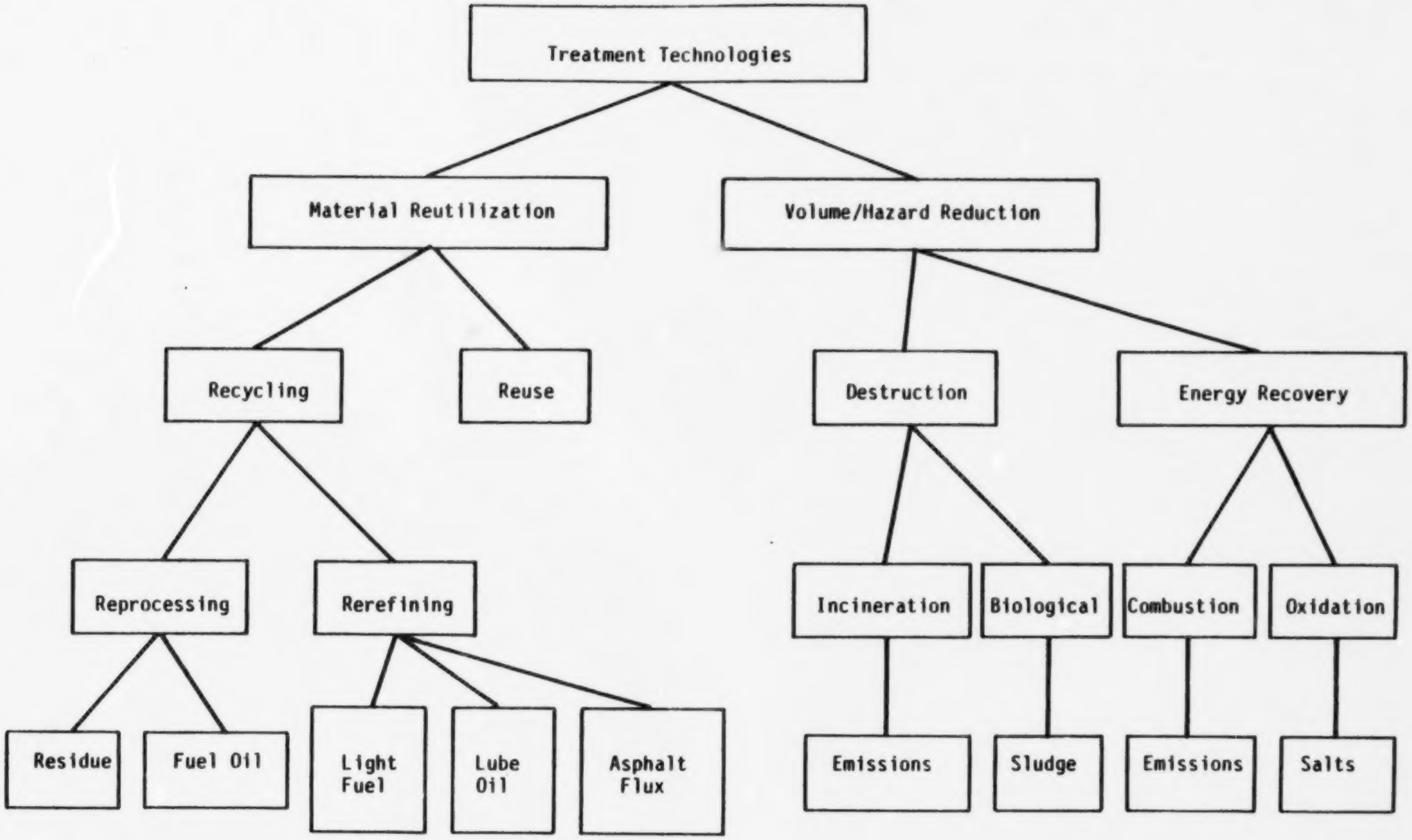
Treatment Technologies
Material Reutilization
Volume/Hazard Reduction
Recycling
Reuse
Destruction
Energy Recovery
Reprocessing
Rerefining
Incineration
Biological
Combustion
Oxidation
Residue
Fuel Oil
Light Fuel
Lube Oil
Asphalt Flux
Emissions
Sludge
Emissions
Salts

Figure 2. Classification of treatment technologies.

involves using the waste in its existing condition, without initial processing. Reuse was once popular for oiling roads and suppressing weeds. These methods proved harmful to the environment and are now illegal in California. Under existing law, used oil must be shown to meet contaminant specifications defined in the California Health and Safety Code (HSC) before it can be reused for any purpose.

Recycling processes treat used oil so that it meets the standards defined in HSC. Recycling includes reprocessing and rerefining. Reprocessing removes some of the solids, organic contaminants, and water contained in the oils. Reprocessed oils are generally used as fuels. Some reprocessing techniques are simple and inexpensive, such as gravity settling and blending. Others are more complex, such as distillation and solvent extraction. There are currently about 300 reprocessors in the U.S. The most commonly used reprocessing steps are:

- Blending: by permitted facilities to meet standards
- Gravitational settling: to remove heavy particulates, tramp oils, and water
- Heating: to facilitate physical separation
- Filtration: to remove particulates down to 2 microns
- Coalescing/skimming: to separate oil from water
- Solvent extraction: to remove ketones, alcohols, and hydrocarbons
- Distillation: to remove water and light fuel

A number of other unit operations are used to a lesser extent, including magnetic separation, centrifugation, hydroclone separation, ultrafiltration, and carbon adsorption. Techniques are chosen based on their cost, efficiency, capacity, and residue production. Reprocessing often produces residues that require disposal. Reprocessing is generally applicable to streams that are not highly contaminated by metals or hazardous organic compounds. Reprocessing techniques are relatively simple and inexpensive to operate. However, they have difficulty in removing metals and additives.

Rerefining involves full scale treatment of used oils to produce lube oils of equivalent quality to virgin oils. In 1960 there were about 150 rerefineries in the U.S. Today, due to stricter regulations and low oil prices, there are only about 15 rerefineries. A number of rerefining processes are commercially used. The general approach to rerefining is to:

1. Remove water by atmospheric distillation
2. Remove volatile organics and solvents by atmospheric distillation
3. Remove additives and sludge by chemical treatment, extraction, vacuum distillation, or membrane processes
4. Remove metals and chlorides by chemical treatment, clay treatment, or extraction
5. Fractionate by vacuum distillation
6. Perform final finishing by hydrotreatment, clay treatment, or vacuum distillation

Processes that generate by-products, such as the acid-clay process, are declining in popularity due to by-product disposal problems. Rerefineries can handle almost all oil wastes, although processing is easier for relatively uncontaminated streams. Products include light ends, which are burned as fuel, lube oil, and asphalt flux. The asphalt flux contains the heavy bottoms, which include the metals and sludge. Rerefining reutilizes used oil for its original purpose and produces little or no waste by-products. However it also requires significant capital investment and has high operating costs.

2.2 Waste Volume/Hazard Reduction

The second treatment category consists of processes designed to reduce the volume of oil waste and the hazard it presents. Thermal techniques are used for waste disposal and energy recovery. Used oils are similar in quality to #6 fuel oil and have relatively high heat contents. This makes them well suited to burning in furnaces and boilers. Before burning, the used oil must be processed to meet HSC standards. Air emissions are also regulated. Pollutants of concern include carbon monoxide, ozone, nitrogen oxides, sulfur dioxide, total suspended particulates, and lead. Virtually any oil waste can be burned. Since used oil has high heat content and usually requires minimal processing to meet standards, combustion for energy recovery is often the most cost effective way to manage used oil. Most reprocessed used oil is burned as bunker fuel on ships. Other commonly used devices include kilns, furnaces, and external combustion boilers. Combustion of used oil replaces fuel that would otherwise have to be purchased. It also reduces waste volume, and destroys hazardous organic compounds. However, combustion renders the oil unusable for its original purpose and can potentially emit air pollutants.

Oil waste can also be incinerated as a hazardous waste. It can be burned without processing in permitted hazardous waste incinerators. This might be warranted for wastes highly contaminated by hazardous organic compounds or when transportation is excessively costly. Incineration can emit toxic chlorine and metal compounds unless sufficient air pollution control equipment is used. Incineration recovers no useful product from the waste. There are currently no regionally permitted incinerators in California, and thus incineration would require out-of-state transportation.

Oxidation techniques can also be used for destruction of oil waste. These techniques use high temperature and pressure to decompose organic compounds and convert metals into easily managed salts. They have been gaining in popularity in recent years.

Biological processes break down hydrocarbons in oil waste. They are commonly used for pretreatment of oily wastewater, and for wastes in which excessive contamination and low oil content makes recovery infeasible. Microorganisms that decompose oil waste are ubiquitous. The two types of biological systems are:

- Solid based systems, including landfarming and attached/entrained growth systems
- Liquid based systems, including biological reactors and lagoons

A number of innovative biological processes have emerged in recent years. Biologically activated carbon treatment (BACT) is one such process. Bioaugmentation is another innovative process, in which microorganisms specifically suited to decomposing a particular waste are added to the system. Virtually all oil wastes are suitable for biological treatment, although high levels of metals or other toxic substances can inhibit efficiency. Some compounds also decompose very slowly. Efficiency depends on the treatment system, oil content, and contaminant concentration.

Biological processes effectively reduce the volume and hazard of oil wastes, and have low capital and operating costs. However, they are slow, require a lot of space, and do not reutilize oil. In addition, they produce a sludge requiring disposal, and some processes, such as landfarming, have a high risk of environmental contamination.

3.0 Factors in Selecting a Treatment Option

The main factors to consider in selecting a treatment option are regulatory compliance, economics, environmental acceptability, and technological capability. Each of these factors should be considered before a treatment option is selected.

Treatment must comply with all regulations. Unless used oil is shown to meet specified standards, it must be managed as a hazardous waste in California. Thus, proper manifests and permits must be obtained for all transportation and treatment. Generators maintain liability for oil waste until it is destroyed or recycled. Thus, by destroying or recycling the waste, proper treatment can ensure that generators manage oil waste legally and can relieve them of liability.

The treatment system must be cost effective. A treatment system should be selected that maximizes oil waste recycling value and minimizes disposal costs of wastes and waste treatment by-products. Economic factors include current market oil prices, capital and operating costs, permitting and insurance costs, collection and transportation costs, and treatment product value.

The treatment system must be environmentally acceptable. The treatment system should minimize exposure of employees to hazardous waste, generate little or no waste by-products, and not emit air, land, or water contaminants. Oil wastes often contain heavy metals and hazardous organic compounds. Generators have both a legal and an ethical responsibility to ensure that these compounds do not contaminate the environment.

The treatment system must also be technologically feasible. The system must produce oil of required purity and composition. It must also have enough capacity to handle the flow of waste to be processed. In addition, the treatment system should be within the technical capabilities of the company operating it. Employees must have the training and experience needed to operate, maintain, and repair the physical and chemical processing equipment.

COMMERCIALIZED TECHNOLOGIES FOR RE-REFINING USED LUBRICATING OIL

by

Dennis W. Brinkman
IITRI/National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005
918/336-2400

INTRODUCTION

There are so many patents on re-refining used oils into lubricants that this presentation could be filled with just a cursory review of each. A recent annotated bibliography provides abstracts for over 250 publications on new processes and over 1200 abstracts on used oil recycling in general that were released since 1970 (1). However, it is felt a more useful format here would be to review a selected few process schemes that have advanced to commercialization and thus are more readily evaluated.

A review similar to this one was provided by Whisman (2) several years ago. However, most of the processes were just being developed at that time. The primary criteria then were high quality lube oil production and generation of either useful or readily disposable by-products. Now, several new plants have been installed, and the selection process determining which general approaches seem most commercially viable has begun to converge. In fact, it is an indication of the maturing of the new technologies that a few variations of one generic technology have accounted for almost all new plants built in the last decade.

TECHNOLOGY DISCUSSION

Thin Film Evaporators. The technology currently attracting the most attention and being incorporated in the most plants revolves around thin-film evaporators (TFE) (3). Processes proposed by several sources are all based on similar designs with a generic outline usually similar to that shown in Figure 1.

Typically, the dehydration and fuel stripping steps are accomplished with very simple flash towers having minimal packing and simple piping. This is possible because of the normally clean cut between most of the contaminants and the lube oil basestock. Figure 2 presents a simulated distillation of a used oil which demonstrates this. Cut points shown on the gas chromatography plot are only one of many possible sets, depending on the fuel and lube oil properties desired. This pair of preliminary process steps (dehydration and fuel stripping) is shared with almost every re-refining technology used or proposed.

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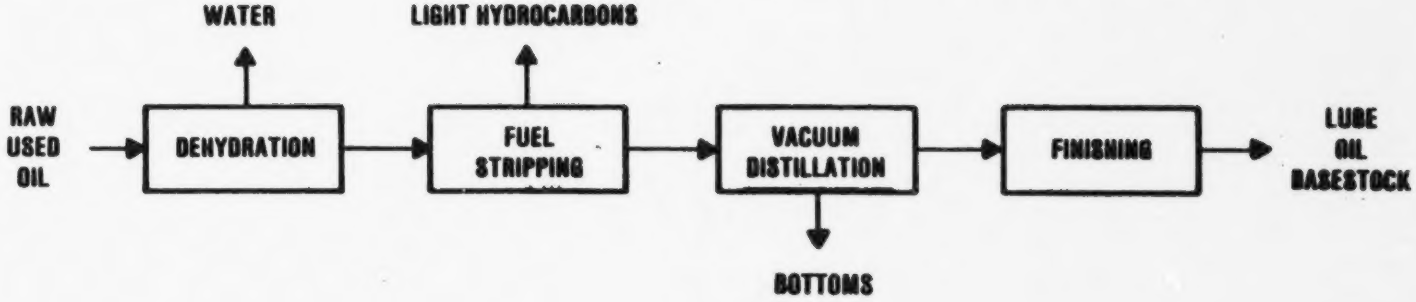
WATER
LIGHT HYDROCARBONS
RAW USED OIL
DENYDRATION
FUEL STRIPPING
VACUUM DISTILLATION
FINISNING
LUBE OIL BASESTOCK
BOTTOMS

FIGURE 1. - Typical Thin-Film Evaporator Re-refining Scheme.

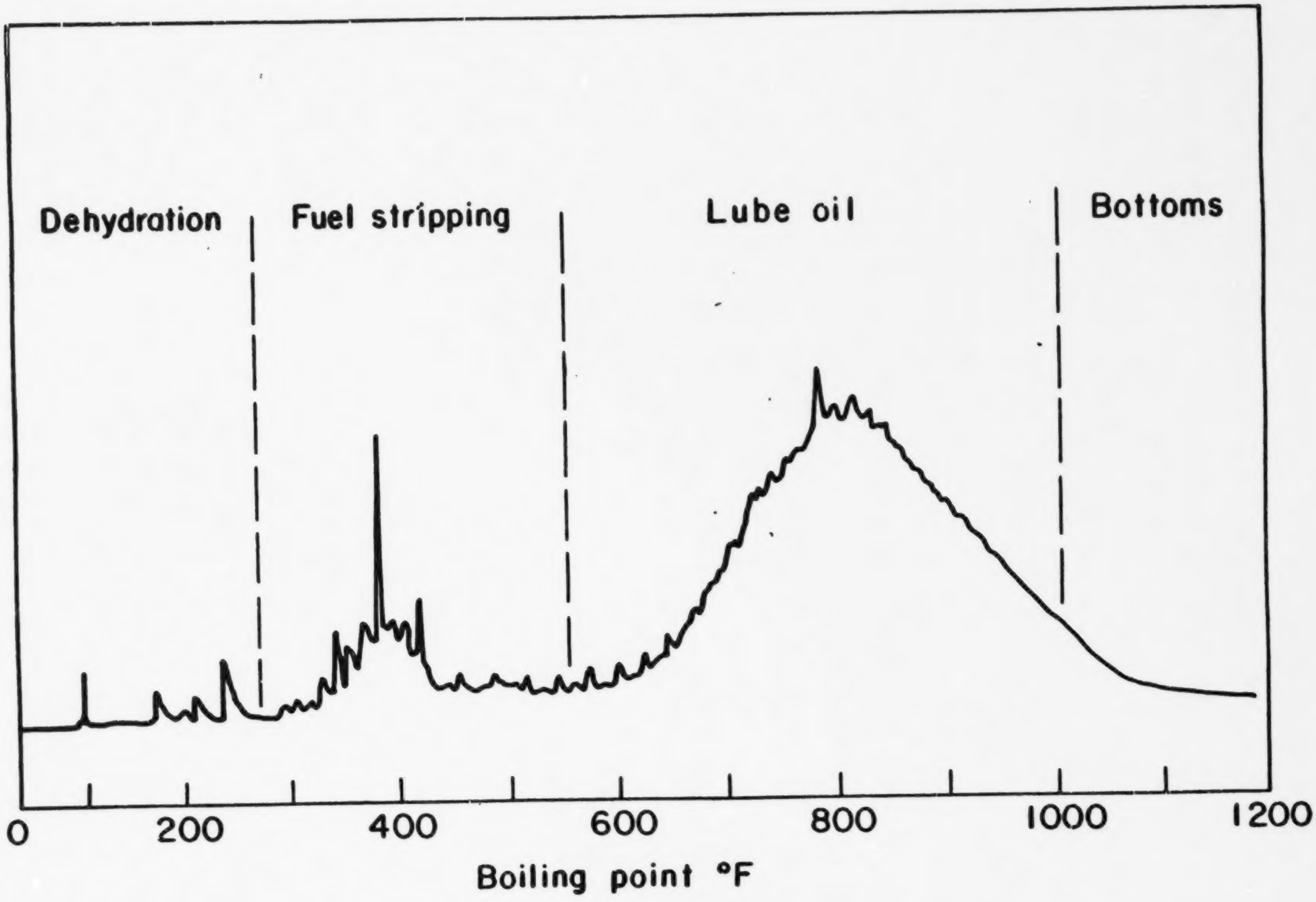

FIGURE 2. - Simulated Distillation Curve Showing Typical Cut Points.

The product from these two steps is usually referred to as a dry or topped oil, and it can be sold as a high quality fuel if the ash content is not too high. The water is usually contaminated with hydrophilic organic compounds such as phenols (4). Depending on local effluent regulations, it may be more economical to treat the water and recycle it as cooling tower make-up water. The light hydrocarbons are of the proper boiling range for gasoline or diesel fuel extenders, but the halogens and other contaminants would tend to cause serious corrosion and erosion problems. Thus, use as a fuel in boiler systems, possibly as the fuel for the re-refinery, is more practical. Even so, they present many internal problems related to corrosiveness and environmental emissions, and some re-refineries elect to dispose of this fraction rather than burn it for fuel.

The vacuum distillation that follows topping can be carried out in several ways. Multiple evaporators can be sequenced to provide several lube oil fractions, or a single unit can be used for a single or multiple passes. In the latter case the bottoms from the previous run become the feedstock for the next higher boiling temperature fraction. A third alternative is to use partial condensation to produce two or more product streams. In this case the vapors are first passed through a condenser held at ambient or higher temperature. The vapors which pass through this initial zone are then condensed with a colder media, such as chilled water. A fourth and final option in commercial use is to produce only one lube cut and blend to the desired viscosity with virgin basestocks. All of these alternatives offer various advantages and disadvantages relative to process flexibility, operational complexity, capital equipment costs, and processing costs.

One prime attraction of the TFE is that it can be retrofitted into older existing facilities. The preliminary and finishing steps are the same as used by almost all processors. A second attraction is the elimination of a pretreatment step thought necessary to prevent coking and fouling in more traditional fractionation towers. This is because the lube oil is maintained at maximum distillation temperature as it flows down the wall in the TFE for only a small fraction of the resistance time typically encountered (a few seconds) in the packing and/or plates of a tower. Commercial operations to date seem to bear out the projected lack of coking problems. A related advantage is that the TFE is much simpler to operate than a fractionation tower. Only one cut point is involved (ignoring the partial condensation option downstream of the vapor outlet); so there are no complex interrelated equilibria that one encounters with several product and reflux streams in a tower. This simplicity also leads to shorter start-up and shutdown times.

The principle disadvantage is the need for several units, or the need for several passes through a single unit, if a slate of several products is desired. The capital and operating costs can become prohibitive.

A second disadvantage is the minimal reflux ratio. Entrainment of higher boiling components in the vapor phase is difficult to counteract in the short pathway provided. However, for making broad lube oil cuts, this is not usually a significant disadvantage.

Clay Only. A commercial process that completely eliminates the distillation step has been in commercial operation from the beginning of the rerefining industry and is still used at a few facilities. This technology relies on large quantities of activated clay (1 to 3 lb/gal) and somewhat higher temperatures than used for clay polishing (100° to 150° F higher) to clean up the dehydrated and fuel-stripped oil. Remarkably, some of the most consistent quality (but not among the higher quality samples) lube oil basestock sampled periodically by the National Bureau of Standards and ASTM over a recent 13-month study period was the product from a facility using this process (5). While this must in part reflect on the expertise of the operators and the uniformity of the feedstock, it certainly demonstrates the potential of this simple operation. Its widest current use is for industrial oils, which often require only dehydration and polishing, but it is used in at least one case for re-refining crankcase oils. It is also used extensively to reclaim contaminated fuels.

The disadvantages of using only clay include a lack of control over the viscosity and boiling range of the product other than through the removal of volatiles during fuel stripping. Thus, the product will tend to be an SAE 20 weight oil with a broad boiling range that may lead to high oil use. Freeze point, pour point, and other properties will have to be controlled through blending with virgin stock or, more likely, through the use of additives. In addition, a rather fixed quantity of oil absorbs onto a given quantity of clay. Thus, the throughput loss increases directly with the increase in clay use. Finally, environmental factors may cause problems, both in terms of disposing of such large quantities of oily clay and in the tendency for some contaminants to emerge from the clay contacting step still in the lube oil. This will be discussed more in a later section.

Chemical Treatment/Hydrotreating. The most unique of the commercial technologies is the Phillips Re-refined Oil Process (PROP) developed and marketed by Phillips Petroleum Company (6). As shown in Figure 3, the typical dehydration/fuel stripping initial steps do not show up here. This is because an aqueous solution of a metal-chelating chemical such as diammonium phosphate is added to the raw used oil, so there is no need to eliminate the water until after this step. The chemical reacts with metal-containing species in a heated reactor and combines with other contaminants to form a sludge which can be filtered out of the oil. After demetallization, the oil is hydrotreated.

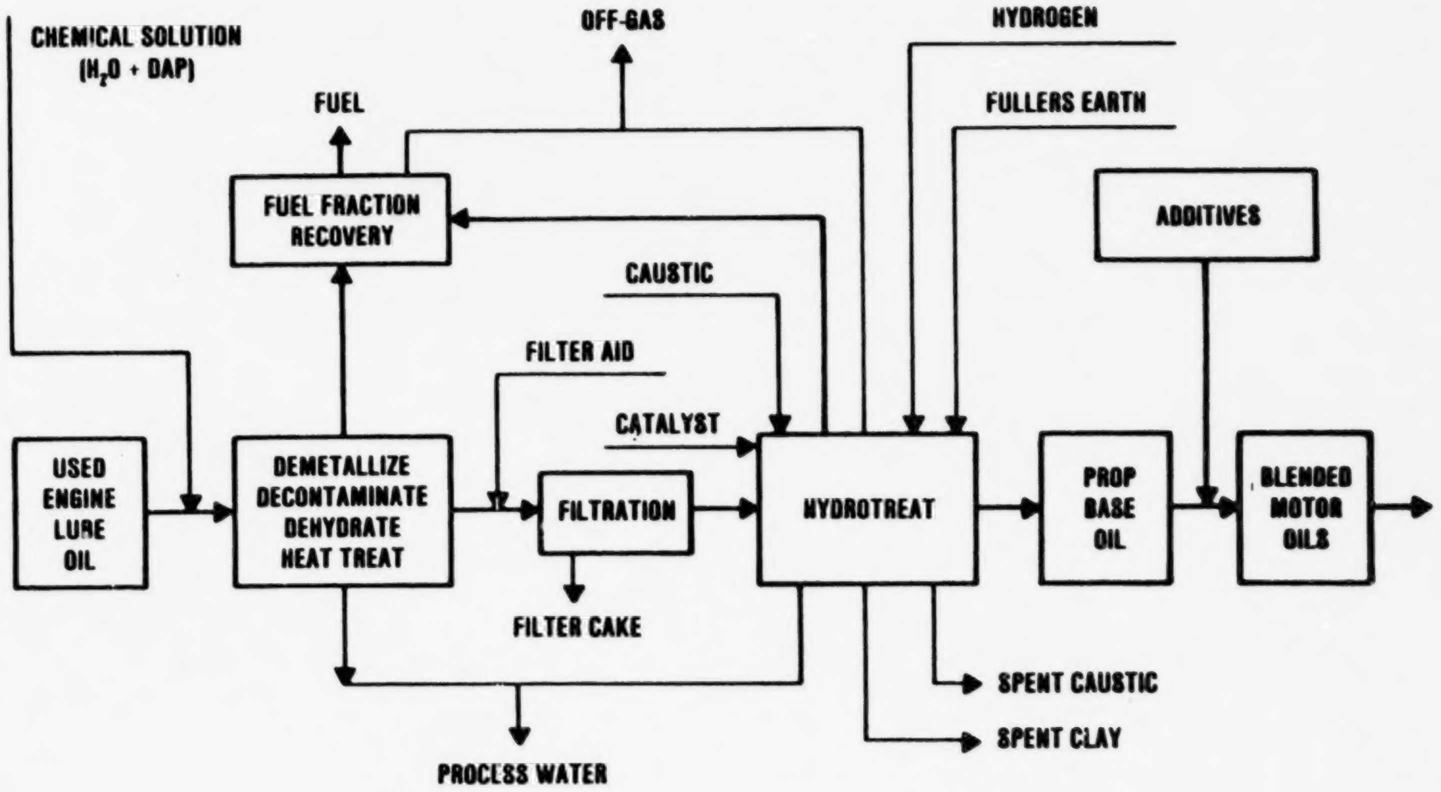
CHEMICAL SOLUTION
(H_2O + DAP)
FUEL
OFF-GAS
HYDROGEN
FULLERS EARTH
FUEL FRACTION RECOVERY
ADDITIVES
CAUSTIC
FILTER AID
CATALYST
USED ENGINE LURE OIL
DEMETALLIZE DECONTAMINATE DEHYDRATE HEAT TREAT
FILTRATION
HYDROTREAT
PROP BASE OIL
BLENDED MOTOR OILS
FILTER CAKE
SPENT CAUSTIC
SPENT CLAY
PROCESS WATER

FIGURE 3. - Re-refining Schematic for PROP Process.

Disadvantages of the basic system caused by the lack of a distillation step are the lack of control over final product boiling range and an unusual level of upgrading the hydrotreating step is expected to provide. The most recent commercial installations of the PROP process have incorporated purchaser-supplied distillation units to alleviate these problems. Such additional units obviously affect the overall economics of the process. Even without this extra hardware, this process is usually considered the most expensive now in commercial operation. Thus, the throughput volume necessary for profitable operation is at least seven million gallons/year. Ten million gallons/year would provide a firmer economic position.

RELATED ISSUES

All of the new re-refineries installed over the last few years have included considerable water treatment, spill containment, and other costly facilities not directly related to producing a quality product. This trend toward greater complexity has forced the industry toward larger volume plants in order to remain profitable. The opposing force to this trend is the cost of expanding to collect larger and larger volumes of used oil. While no generalization can be made for every part of the country, the optimum size re-refinery for the next generation plants would seem to be in the 10-15 million gallons/year range. This is a significant quantity to locate and secure on a regular basis. Thus, the establishment of a reliable feedstock supply is probably the most critical consideration. Under capitalization is the second biggest problem. Re-refining has typically been a small, family-type business. The need for complex equipment and large volumes has forced this to change.

CONCLUSIONS

It is impossible to say which technology is the best. Much depends on the processing flexibility desired. If a wide variety of feedstocks, such as solvents, sludges, and contaminated crude oils, are to be processed in addition to the re-refining of used lube oil, then a more flexible and complex system will be required.

Similarly, the future of re-refining is difficult to predict. Pending environmental regulations will help define some testing requirements and contaminant limitations. However, the economics of re-refining are still dictated by the price paid for used oil to be burned as a fuel and the price of virgin lube oil basestocks. The re-refiner has little control over either.

It has been shown that re-refining would be a useful contribution to energy and resource conservation for this and any other country (7). It remains to be seen whether it will be attractive to a significant number of individual investors.

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REREFINING CASE STUDY: EVERGREEN OIL REREFINERY

By John Fok, Evergreen Oil, Inc.

1.0 Background

Growing environmental concerns in industrialized countries have triggered a shift from burning towards rerefining. One of the most aggravating problems with used oil burning is the emission of toxic, nondegradable compounds. In one study, burning used oil with PCB concentration of 1.5 ppm in a 2 MW furnace resulted in emissions of 146 ng/m^3 polychlorinated dibenzofurans (PCDF) and 60 ng/m^3 polychlorinated dibenzodioxins (PCDD). In Vienna, waste lube oil with 47 ppm PCBs was burned in a 7 MW unit. Emissions were 375 ng/m^3 PCDF and 73 ng/m^3 PCDD (1,2). These investigations indicate that during used oil burning the emissions of dioxins and furans are not solely caused by PCBs. They are mainly influenced by the presence of chlorinated hydrocarbons and inorganic chlorine compounds. This conclusion has been confirmed by other publications (3) which state that PCDD and PCDF emissions occur because of incomplete combustion of chlorinated hydrocarbons. These compounds include PCBs, chlorinated benzenes, and chlorinated inorganic compounds. Because used oil burning can emit dangerous compounds, stringent legislation became a prime objective in Austria, which resulted in the "Altolgesetz" (Waste Oil Act) of September, 1986.

This type of legislation influences rerefining technology acceptability. Processes removing chlorinated hydrocarbons are encouraged. One rerefining technique which ensures the degradation of chlorinated hydrocarbons is hydrofinishing of used oil distillates. This technique is used in the KTI Process. It has been very successful in commercial installations.

2.0 Process Description

The KTI Process consists of several steps. Each step serves as a "sieve," separating a specific group of contaminants. Contaminants are classified by their physical and chemical properties and concentration.

The process steps used to recover or rerefine the lube oil are:

A. Separation of the lube oil components from used oil by physical processes such as vaporization, distillation, and stripping.

B. Finishing of the separated lube oil by hydrotreating.

Most non-lube oil components have different boiling ranges than lube oil. Only fatty acids, esters, some chlorinated compounds, and some additives have similar boiling ranges. These compounds remain mixed with lube oil after distillation. They are removed in the finishing step.

2.1 Separation of Light Components

Light components are separated by vaporization and stripping. In the first step, water, gasoline, and light boiling components such as trichloroethylene are removed. This is done by atmospheric flash evaporation at approximately 150 °C. Light boiling components include gasoline, solvents, and glycol. In the second step, dewatered spent oil is further distilled to strip off gasoil (diesel fuel). Fractionation is used to separate gasoil from lube oil. This minimizes lube oil loss. Distillation is performed under vacuum at about 270 °C.

2.2 Separation of Heavy Components

Lube oil components and co-boilers are separated by flash distillation. In the third process step, heavy components are concentrated in a residue stream. Due to fairly high solids content and high hydrocarbon molecular weight, vacuum distillation is carried out in a special wiped film evaporator. Temperatures above 340 °C crack lube oil components. This avoids fouling of heat transfer surfaces. The heavy components consist of additives, metals, and degradation products. They are concentrated in asphalt flux, which is used as roofing material.

2.3 Hydrofinishing/Fractionation

In the fourth step, contaminants which boil in the same range as lube oil are removed by catalytic hydrogenation. The lube oil distillate is purified by treating with hydrogen. This treatment removes the co-boiling impurities that distill over with the lube oil fractions. These impurities are primarily chlorine, oxygen, and nitrogen containing organic compounds. Upon hydrogenation, they form gasoil, ammonium chloride, and water. A part of the organic sulfur is also removed and forms hydrogen sulfide. Light gaseous paraffins are formed. The hydrofinished lube oil is separated from the gaseous products by flashing at low pressure. It is then fractionated into a gasoil fraction and a lube oil fraction. The lube oil fraction is further split into heavy and light products.

2.4 Characteristics of the KTI Process

Feedstock Flexibility

To be successful, a rerefining process must have great flexibility in dealing with contaminants. The KTI Process features high selectivity for separating hydrocarbons from non-hydrocarbons.

High Product Yield

Increasingly complex lube oil additives have made conventional used oil reprocessing techniques, such as the acid/clay process, more difficult to operate. This has reduced lube oil yield. Reduced yield is one reason for the recent decline in rerefining. The KTI Process recovers over 95 percent of lube oil components. This makes the KTI Process significantly more economical than conventional processes.

Product Quality

Years of operational experience have shown that the KTI Process produces a product equivalent to virgin lube oil. Product quality is very important for marketability and consequently for the success of a rerefinery. Table 1 shows typical characteristics of rerefined and virgin lube oils. Of most importance is that rerefined lube oils retain their original viscosity and

Table 1. Product Quality Data for Virgin and Rerefined Oils

	KTI Rerefined Oil		Virgin Base Oil
	Light Neutral	Heavy Neutral	150 Neutral
Elements:			
- Sulfur, mass %	0.3	0.4	0.32
- Chlorine, mg/kg	10	10	-
- Other metals, mg/kg	1	1	4
Color (ASTM)	L 1.5	L 1.5	L1.5
Viscosity, cm^{2}/s (40 $^{\circ}$F)	13.05	95.28	30.08
Viscosity Index	98	99	107
Conradson Carbon mass %	0.01	0.02	0.07
Total acid no. mg OH/g	0.01	0.03	0.05
Unsulphonated res. vol. %	96	98	94
Oxid. Stability IP40			
Ratio kin. viscosity			
at 40 $^{\circ}$C	1.12	1.20	1.36
RCR increase, mass %	0.42	0.68	1.00

viscosity index properties. Rerefined lube oils also show excellent oxidation stability and good response to oxidation inhibitors.

Destruction of PCBs, PCDDs, and Furans

Operating experience and laboratory tests have shown that PCBs, PCDDs, and furans present in the rerefining distillates react in the hydrofinishing section. They form non-polluting hydrocarbons and HCl.

No Hazardous By-products

By removing hazardous and bulky by-products, handling and disposal costs are minimized and product loss is avoided. Streams generated during the process include:

Light Boiling Hydrocarbons: While chlorine content in the light boiling fraction is great concern to many rerefiners, the KTI Process uses light boiling hydrocarbons as process fuel. Light hydrocarbons are burned in a special incinerator.

Distillation Residue: Additives, ash components, and sludge containing metals and other inorganic contaminants are concentrated in a highly viscous, bituminous product. Tests have shown that no metals leaching occurs. This product is suited for use as an asphalt extender.

Wastes: No solid by-products other than spent catalysts are generated.

Effluents: Waste water is produced by the vacuum system as drive stream condensate, by the fractionation section as stripping steam condensate, and by the hydrofinishing section as wash water. This waste water is subject to local regulations. It is treated to standards which are accepted by the municipal waste water system.

3.0 Commercial Status

KTI has significant experience in the reprocessing and rerefining of used lubricating and industrial oil. Rerefining plants utilizing the proprietary KTI Process commercially operate in Aspropyrgos, Greece; Bizerte, Tunisia; Newark, California; and at the largest rerefiner in the world, Dr. Anton Maier AG, Germany.

In 1982 the first rerefining plant to utilize the KTI Process was completed. This 20,000 metric ton per year rerefinery has produced premium grade lubricating oils since that time. It was designed and constructed on behalf of VAROIL S.A. and is located in Aspropyrgos, Greece. The most recent KTI rerefinery was built in Newark, California.

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Thermal Treatment Options
by
Micheal Zimmer
SYSTECH Corporation

I Current regulatory structure on thermal treatment

II Estimated amount of used oil treated by thermal methods in California

III Review of thermal treatment methods

IV Benefits of thermal treatment

V Description of SYSTECH's system

VI Conclusions: Present and Future

Thermal Treatment Options for Used Oil

The Federal government under the watchful eye of the EPA has addressed the management of hazardous waste via the Resource Conservation and Recovery Act of 1976 (RCRA) and the 1984 amendments to RCRA. RCRA's national program is vast yet it's bottom line is simple," cradle to grave".

In 1978 the EPA intended to list used oil as a hazardous waste on the premise of it's toxicity. It also intended to regulate oil when it was incinerated or burned as fuel. Due to adverse commentary by industry and oil processors EPA deferred listing used oil. However, if used oil exhibited one of the four characteristics and was disposed, accumulated, stored or treated used oil would therefore be regulated. With little to no enforcement and accountability used oil was kept on the sidelines of the regulations.

It wasn't until the 1984 amendments to RCRA that used oil started to feel the pressure from the regulations. In 1985 EPA issued its intention to list used oil as a hazardous waste. EPA evaluated used oil against the criteria for listing hazardous waste and determined that used oil presented a substantial threat to human health and the environment when improperly managed.(1) EPA examined hundreds of used oil samples. EPA concluded that a number of toxic constituents were present at levels of regulatory concern. In November of 1985 EPA finalized burning of used oil regulations in non-industrial boilers and the first used oil fuel specification was establish. Used oil meeting this standard would not be regulated by RCRA. Oil not meeting this standard was called off-specification used oil and could only be burned in boilers and industrial furnaces which had pollution control devices and made notice to EPA. A tracking system was established from point of generation to the final burner. Storage and treatment would also be regulated.

California has always treated used oil as hazardous. However, California passed its first used oil law in September 1986. SB86 revised and enacted provisions for regulations of used oil. SB86 defined "recycled oil", "used oil" and would require that used oil, except used oil meeting specific standards, be handled and managed as a hazardous waste. This bill patterned itself after EPA except that California law appears to be more stringent.

California's largest waste category is 221 (waste oil and mixed oil). In 1987, approximately 400,000 tons of used oil was tracked via the California hazardous waste manifast. This 400,000 tons equates to 80 million gallons. The major portion of this used oil is blended and burned at our west coast harbors as fuel. DOHS believes this percentage of blended used oil burned at our harbors could be as high as 70 percent. My option is that used oil going to and from the reprocessors lacks quality testing. Certainly if a lack of quality testing at the reprocessor than obviously what kind of quality testing is preformed at the harbor. I ask, "Have you ever heard of a truck of used oil being rejected at the harbor?"

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(1) USED-BUT USEFUL: A Review of the Used Oil Management Program in New York State, October 1986, p.31.

Historically used oil has caused plenty of problems for industry and our environment when not managed properly. Times are changing because the cost of crude oil is at its lowest cost level in ten years. Regulated oil facilities will be a reality in the near future.

Currently the reprocessors are having hard times because it cost dollars to process waste and to be regulated. At the current prices on crude, the reprocessors are charging for processing used oil. This trend is now a reality across this United States of America. A New York used oil study in 1986 states the oil situation clearly. I quote, "of the used oil entering the system a vast majority is burned as fuel. Many collectors and reprocessors sell their used oil as fuel, with little or no processing to remove toxic contaminants".(2) This study further states that additives in oil can account for ten to twenty percent of the product. Our new fuel efficient combustion engines are demanding higher quality specification oil which means even more complex blends. The combustion engine of the future will burn cleaner fuels and will have computer fuel injection systems because we the public demand less maintenance, higher performance and greater fuel efficient cars. This can only mean two things. More reprocessing to get the additives out or burn this material in an approved permitted industrial furnace that will destroy the additives. These furnaces have good pollution control devices to greatly minimize the risk of burning this material for energy recovery.

Some of the thermal treatment options are the industrial boilers, utility boilers and industrial furnaces. At the top of this list is the industrial furnaces. These furnaces can be cement kilns, lime kilns and other large energy intensive rotary kilns. The most extensively tested industrial furnace is the cement kiln. Couple this with its manufacturing of a product and you have the makings of a superior existing furnace capable of burning used oil. In another study by New York State I quote, "Tests conducted at a number of

(2) USED-BUT USEFUL: p. 1.

facilities in the United States, Canada and Europe have demonstrated that cement kilns can safely destroy almost all types of organic wastes, while providing the added benefit of energy that would otherwise be discarded".(3)

The State of California has tested the National Cement Plant (formally General Portland Inc.) cement kiln near Gorman, California, twice. This was a cooperative effort of EPA, DOHS, CARB, KCAQCD and the Cement Plant. Test burns were performed in the spring of 1982 and the fall of 1984. Very little testing has taken place at aggregate, lime and asphalt rotary kilns. By far, all the studies to date show that the superior temperatures, retention times and turbulence in the cement kiln exceeds all others.

The destructive rotary kilns of Chemical Waste Management (CWM), Rollins and Ensco certainly have their place in waste management. These kilns have proven their ability to destroy waste. The industrial furnaces handle more of the higher BTU and Liquid waste while the destructive kilns seek both high and low BTU along with higher viscosity materials in the form of sludges and solids.

The industrial and utility boilers have not had the proven testing of the other thermal treatment facilities. This situation exists because used oil has been kept on the sidelines of RCRA all these years. The future for used oil will be quality control procedures, testing materials and risk analysis when burning used oil for energy recovery. Also the reprocessor will need to bring their facilities up to the standards of RCRA and show their sites are environmentally sound.

Three years ago the steel mills in the east were burning blended fuels. The EPA wanted the steel mills to do tests burns and get permits for storage. Basically the EPA wanted the steel mills to follow the regulations and the lead of a few permitted and regulated cement kilns. The steel mills declined an EPA invitation to follow in the footsteps of a few state of the art waste management processes all ready in place. This "No" from the steel mills put millions of gallons of blended fuels into a market that lacked capacity. Today there are more facilities on line and capacity is not a problem except in selected areas. The United States to a great extent has lost our great steel industry. For this reason our country needs to support our remaining basic industries. Our industrial furnace companies are our basic foundations to our industrial growth. If the United States loses these industries to imports, it will also lose one of the best industries to handle the waste needs of and industrial America. Look around, Southern California has some very large cement project in progress now. The Century Freeway, Metro-rail, freeway walls, dividers and expansion, new and replacement sewer projects, airport expansion and our strong building industry. The LA Times reported recently that our cement imports are at twenty-five percent. I support the "Made in the USA". It would be a good feeling to know that the large cement project were made with cement manufacture in Southern California. We all know the out come of our steel industry. Lets support our basic industrial industries. I challenge our politicians, public officials and industrial representatives to keep a watchful and informed position on the impact of imports, especially our basic building block industries.

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(3) Hazardous Waste Incineration: The Cement Kiln Option, New York State, December 1987, p. 1.

There are many benefits of thermally destroying our hazardous waste. Two major benefits come to mind right away. First, EPA has stated that the priority treatment standard for organic liquids, sludges and solids is incineration or thermal treatment. The other is that thermal treatment or incineration will reduce or eliminate the ball and chain of RCRA which is "Cradle to Grave". Incineration or thermal treatment is a proven and tested technology. Under RCRA the cement kiln meets the standard of 99.99 DRE.

SYSTECH Corporation was founded in 1969. SYSTECH is a nationally recognized and respected company with almost twenty years of practical experience in environmental and waste management technologies. SYSTECH's major goal is the safe handling and disposal of industrial hazardous waste by recovering resources from these waste.

SYSTECH began working with our General Portland subsidiary in 1979 on a supplemental fuels program for the firm's cement kilns. Development and expansion of this program has continued, and is a primary strategy in our ongoing drive to substantially reduce costs throughout our cement manufacturing operations.

SYSTECH operates as a separate company with its own Board of Directors. It has supplemental fuel facilities and provides waste materials Lafarge cement plants in Alpena, Michigan; Demopolis, Alabama; Fredonia, Kansas; and Paulding, Ohio. Three additional Lafarge cement facilities are presently in the planning and permitting process to allow for the use of waste fuels. SYSTECH also supplies waste-derived fuels to the National Cement's plant in Lebec, California, and Lone Star Cement's plant in Greencastle, Indiana. Three other non-Lafarge cement plant projects are in the planning stages.

SYSTECH selects, analyzes, receives and blends liquid wastes from many diverse industries. These wastes, primarily spent solvents, contain heat energy which is released when burned. Thus, when these wastes are utilized as supplemental fuel in cement production, they are not only destroyed but their heat energy is recovered. The extreme heat and retention time inside a cement kiln ensure that wastes are thoroughly destroyed. In fact, extensive testing has shown that the thermal environment in cement kilns is more intense and waste destruction more complete than in most industrial incinerators.

In the supplemental fuel program, wastes are used to replace a significant portion of more expensive conventional fuels normally used in the energy-intensive cement manufacturing process. This technology, therefore, reduces our manufacturing costs, conserves valuable non-renewable energy, provides a safe and cost-effective solution to the disposal problems of waste-generating industries, and protects the environment through the safe and complete destruction of hazardous and nonhazardous wastes.

Each supplemental fuel installation is permitted by appropriate local, state, and federal agencies. SYSTECH identifies prospective waste generators and analyses the materials at the point of origin. If they meet SYSTECH's specifications, wastes are delivered to a supplemental fuel installation by specially permitted and licensed transportation companies.

SYSTECH operates a dedicated analytical laboratory at each facility. Here SYSTECH personnel also screen all incoming materials before off-loading into storage tanks. If an incoming shipment fails to meet required standards, it is returned to the generator.

The waste material is tested again before it is approved for transfer to the cement kiln.(4)

In conclusion, the following scenarios are in progress or will be in progress in a few years:

-The existing industrial furnace facilities can meet industries waste capacity.

-The cement kiln is the best proven and tested industrial furnace existing now.

-Waste management and waste minimization will lead industry to a more environmentally safe future.

-Off specification used oil will be regulated and managed in an environmentally safe way.

-Reprocessor and refiners will be regulated and held accountable for past and future operations at their facilities.

-The energy value of used oil will never be able to offsite the cost of operations of a regulated facility.

-Used oil will be subjected to a greater testing and evaluation based upon increasing scientific analysis and risk management.

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(4) Lafarge Corporation: Third Quarter Report 1987

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-Used oil will follow the same course as spent non-halogenated solvents do now.

-Industry and the public will be willing to pay a cost for recycling when the regulatory burden is clearly understood.

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A LOOK AT OILY WATER RECYCLING IN CALIFORNIA: DEMENNO/KERDOON'S FACILITY

Andora Sprecher
DeMenno/Kerdoon, Inc.
Compton, California 90222

BACKGROUND

Used oil and oily water are considered in California as hazardous wastes, to be handled, stored and used in accordance with certain provisions and regulations adopted by the State Department of Health Services. The Used Oil Recycling Act prescribes requirements regarding the collection, storage, recycling, use and diposal of used oil. Senate Bill 86 (Presley, 1986), revised these provisions and enacted other provisions for the regulation of used oil as defined. This law defines "recycled oil" and requires that used oil, except used oil meeting specified standards, be handled as a hazardous waste. In any action to enforce this new law, the burden is on the generator and user of the used oil to prove that the oil met those standards and criteria.

This presentation will provide citations of the new law most pertinent to generators, a description of oils and oily water treatment and recycling at Demenno/Kerdoon's facility, and a discussion of the generator's responsibility to determine if his wastes are hazardous and his subsequent liability under the Resource Conservation and Recovery Act (RCRA).

Article 13, Chapter 6.5, Division 20, Health and Safety Code:

Beginning with Section 25250.1, key terms are defined:

(a) "Used Oil" means any of the following:

(1) Any oil that has been refined from crude oil and has been used, and, as a result of use, has been contaminated with physical or chemical impurities.

(2) Any oil that has been refined from crude oil and, as a consequence of extended storage, spillage, or contamination with nonhazardous impurites such as dirt and water, is no longer useful to the original purchaser.

(3) Spent lubricating fluids which have been removed from an engine crankcase, transmission, gearbox, or diffential of an automobile, bus, truck, vessel, plane, heavy equipment, or machinery powered by an internal combustion engine.

(4) Spent industrial oils, including compressor, turbine, and bearing oil, hydraulic oil, metalworking oil, refrigeration oil, and railroad drainings.

(5) Contaminated fuel oil with a flash point greater than 100 degrees F.

"Used oil" does NOT include oil which has a flash point below 100 degrees F or which has been intentionally mixed with hazardous waste, other than minimal amounts of vehicle fuel.

"Used oil" does not include oil which contains polychlorinated biphenyls (PCBs) at a concentration of 5 ppm or greater.

"Used oil" regulated by the department shall be managed as a hazardous waste until it has been recycled or disposed of.

"Used oil" shall NOT be disposed of to sewers, drainage systems, surface or groundwaters, watercourses, or marine waters, by incineration or burning as fuel, or by deposit on land.

(b) "Board" means the California Waste Management Board.

(c) "Recycled oil" means any oil, produced from used oil, which has been prepared for reuse and which achieves minimum standards of purity, in liquid form, as established by the department. The following standards of purity are in effect unless the department, in regulation, established more stringent standards:

(1) Flash point: minimum standards set by the American Society for Testing and Materials for the recycled products.

(2) Lead: 50 ppm or less.

(3) Arsenic: 5 ppm or less.

(4) Chromium: 10 ppm or less.

(5) Cadmium: 2 ppm or less.

(6) Chlorides: 3,000 ppm or less.

(7) PCBs: 5 ppm or less

Compliance with these standards shall be determined in accordance with the procedures in Article 11, Section 66693, of Title 22 or the California Code of Regulations.

(d) The standards set in the above section include the only concentrations allowed above the criteria adopted pursuant to Section 25141.

(e) Used oil which meets the standards set in (c) above and the criteria in (d) above, is not regulated by the department. Any person who generates used oil and who claims that the oil meets those standards and criteria, shall notify the department of its claim and shall comply with the testing and recordkeeping requirements of Section 25250.19 prior to its reuse. In any action to enforce this article, the burden is on the generator and user of the used oil to prove that the oil met those standards and criteria.

Exemptions:

(a) Any virgin oil product or partially refined product which has not been previously used, which has become contaminated with nonhazardous impurities such as dirt or water, and which has been returned to bulk storage by the product's manufacturer, transporter, or wholesaler for gravity separation of contaminants is exempted from this article.

(b) Any petroleum product which becomes contaminated with any other petroleum product during refining, transportation by pipeline, or storage and which remains usable as a refinery feed stock or as a refinery fuel, is exempt from this article.

DEMENNO/KERDOON: A TOTAL APPROACH TO RECYCLING

The Water Phase

DeMenno/Kerdoon's technology brings the water phase to below 10 ppm of oil and grease. The systems utilized in the water-treating phase include the following:

(a) Oil, water and solids separation

(b) PH neutralization

(c) Chemical flocculation and demulsification

(d) Dissolved Air Floatation (DAF)

(e) Volatile organic removal

(f) Granulated activated carbon adsorption

The agency responsible for monitoring this phase is the Los Angeles County Sanitation District with which DeMenno/Kerdoon is fully permitted. Refer to the Process Flow Diagram on Page 6 for more information.

The Oil Phase

DeMenno/Kerdoon utilizes the highest degree of technology in converting the oil phase into finished petroleum products which include: naphtha, lube oil, marine diesel, flux, and asphalt. The systems and facilities included in the refining and processing of used oils include:

(a) Chemical dehydration

(b) Atmospheric distillation

(c) Vacuum distillation

(d) Distillate treating

(e) Lube distillate treating

(f) Asphalt manufacturing

The agencies with which DeMenno/Kerdoon is permitted include:

(a) Department of Health Services

(b) Environmental Protection Agency

(c) California Waste Management Board

(d) South Coast Air Quality Management District

Refer to the Process Flow Diagram on Page 6 for more information.

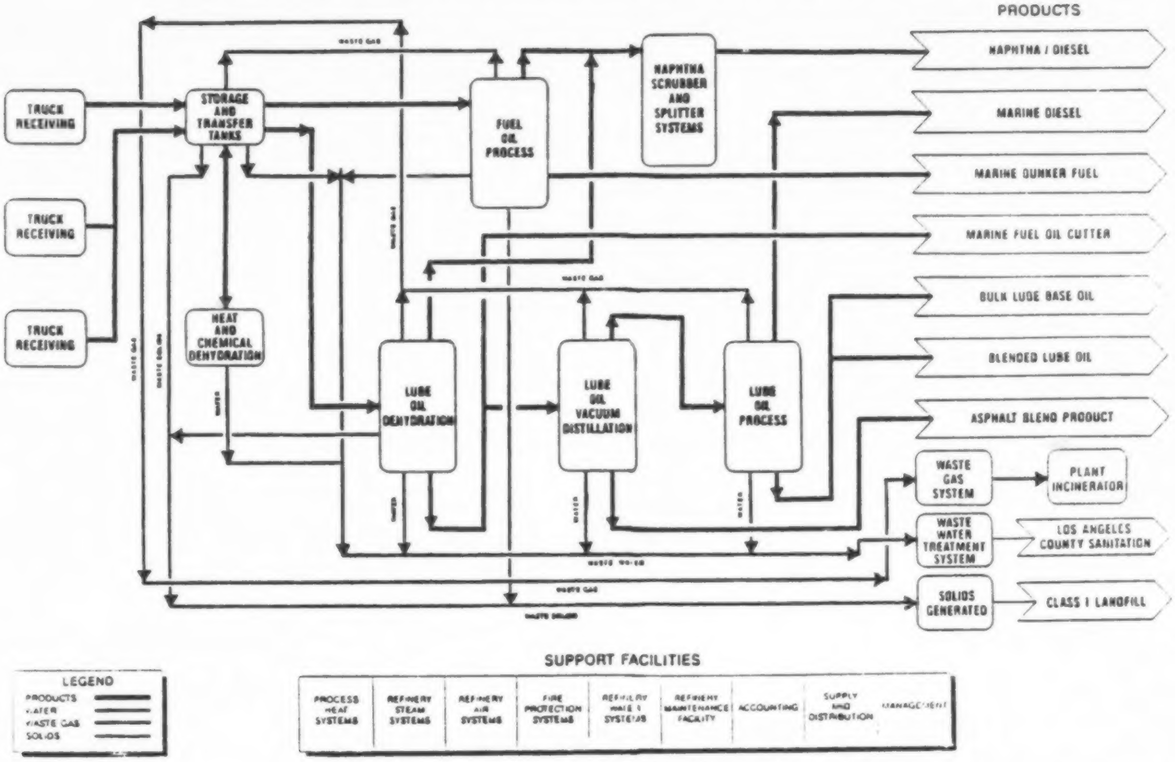
Department of Health Services' Grant to DeMenno/Kerdoon

The Alternative Technology and Development group of the DOHS has granted the first funding ($23,000) of a $500,000 grant for the design of a LUWA Thin-Filmed Evaporator for waste reduction. This unit will allow a greater recovery of naphtha for eventual processing and sale in conformance with waste minimization laws and SB 86.

GENERATOR RESPONSIBILITIES

Only you, the generator, have the responsibility of determining the hazardous nature of your wastes. You need to ensure that when you either sell (as in the case of some contaminated products) or recycle your used oils and oily water offsite, that you utilize a facility that can treat both phases to the statutory levels described previously. Some facilities only use gravity separation or blending as a means of "treatment" prior to the sale of oils for use in industrial and marine boilers. Some facilites only treat the water fraction, then sell or dispose of the oil fraction somewhere else. If you are not aware of where that "somewhere else" is, you have increased your potential liability. When you manifest your wastes to DeMenno/Kerdoon, BOTH phases are treated to within permitted levels, giving you, the generator, greatly lessened liability.

DEMENNO / KERDOON CONDENSED PROCESS FLOW DIAGRAM


PRODUCTS
TRUCK RECEIVING
TRUCK RECEIVING
TRUCK RECEIVING
STORAGE AND TRANSFER TANKS
HEAT AND CHEMICAL DEHYDRATION
FUEL OIL PROCESS
NAPHTHA SCRUBBER AND SPLITTER SYSTEMS
LUBE OIL DEHYDRATION
LUBE OIL VACUUM DISTILLATION
LUBE OIL PROCESS
WASTE GAS
WASTE SOLIDS
WATER
NAPHTHA / DIESEL
MARINE DIESEL
MARINE BUNKER FUEL
MARINE FUEL OIL CUTTER
BULK LUBE BASE OIL
BLENDED LUBE OIL
ASPHALT BLEND PRODUCT
WASTE GAS SYSTEM
PLANT INCINERATOR
WASTE WATER TREATMENT SYSTEM
LOS ANGELES COUNTY SANITATION
SOLIDS GENERATED
CLASS I LANDFILL
LEGEND
PRODUCTS
WATER
WASTE GAS
SOLIDS
SUPPORT FACILITIES
PROCESS HEAT SYSTEMS
REFINERY STEAM SYSTEMS
REFINERY AIR SYSTEMS
FIRE PROTECTION SYSTEMS
REFINERY WATER SYSTEMS
REFINERY MAINTENANCE FACILITY
ACCOUNTING
SUPPLY AND DISTRIBUTION
MANAGEMENT

The Nations Largest Petroleum Recycler

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GIBSON

GIBSON OIL & REFINING CO., INC.

RECYCLING: THE ULTIMATE SOLUTION

by

Lucas T. Dobrzanski, President
Gibson Oil & Refining Co., Inc.
Bakersfield, California

John R. Mullin, President
Fluid System Products, Inc.
Bakersfield, California

Presented At:
OIL WASTE MANAGEMENT ALTERNATIVES SYMPOSIA
Sponsored By:
California Department Of Health Services
In Cooperation With:
United States Environmental Protection Agency

A Subsidiary of V.L.S., Inc.

2101 Webster St., Suite 1700
Oakland, CA 94612
415/446-7777 Telex: 338-139

3121 Standard Street
Bakersfield, CA 93308
805/327-0413 Telex: 494-9206

PHYSICAL TREATMENT OF USED OIL/OIL WASTE

I. Introduction

"Oil and water do not mix"! Truth or fiction? Many people believe that water and oil do not mix, at least until they try to separate them. The following is a brief overview of physical treatment processes used for the separation of water, oil and solids. The benefits of recycling used oil and waste oil are also discussed.

II. Benefits Of Physical Treatment

A. Concentration of contaminants in one stream

Recovery of nonhazardous water and/or oil streams leaves hazardous contaminants in one stream, which is easier and less costly to process.

B. Volume reduction of disposal stream

Recovery of non-hazardous component streams minimizes volume of stream to be treated.

C. Separation of hazardous stream into non-hazardous components

Recovered non-hazardous water streams may be reused or disposed of in the manner of normal waste water (sewer, non-hazardous injection well, etc.). Recovered oil streams may be reused, recycled or sold.

D. Environmental Benefits

Minimization of waste streams and reuse of recyclable components benefits the natural environment, the social environment, the waste generator and the end users of the recycled streams.

III. Review Of Physical Treatment Technologies

A. Theory of Physical Treatment

1. Gravity separators

(a) Gravity settling

Non-emulsified water and oil, as well as non-entrained solids will naturally separate due to specific gravity differences between the phases. This primary settling generally takes places in a quiescent storage container or settling device.

(b) Enhanced settling

Enhanced settling is accomplished by the application of centrifugal force to the liquid in excess of natural gravity. This is done to hasten the separation of the the phases. This is typically performed in centrifuges or "cyclonic" separators which cause the liquid stream to spin at high velocity.

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2. Coagulation & flocculation

Nearly all dispersed particles in an aqueous liquid have an electrically charged surface. Coagulants are usually low molecular weight compounds which become ionic when dissolved in water. This ionic charge neutralizes the "Zeta Potential" of the dispersed particles, allowing the particles to naturally agglomerate into larger, heavier particles with a greater tendency to settle. Flocculants are generally synthetic polymers which are also ionic when dissolved in water. Flocculants are typically very large molecules which adsorb the coagulated particles and add their own mass to produce very large "floccules" of particles which are easily separated from the liquid, either by settling or by flotation in an air or gas flotation device.

3. Emulsion/reverse emulsions

Emulsions are extremely stable dispersions of water in oil, where oil is the continuous phase. Reverse emulsions are extremely stable dispersions of oil in water where water is the continuous phase. Emulsions and reverse emulsions are caused by excessive "interfacial tension" (IFT) between the water and oil phases which overcomes the natural immiscibility of oil and water and inhibits separation of the respective phases. High IFT may be exacerbated by the presence of dispersed solids which may contain emulsifiers on their surfaces or by liquid emulsifiers such as detergents, surfactants, dispersents, etc. The breaking of emulsions and reverse-emulsion involves the proper use of "interfacial tension" reducing agents, heat, agitation and settling.

4. Filtration

Filtration may be defined as the separation of undissolved, particulate, suspended solids from a fluid mixture by passage of most of the fluid through a media or membrane that retains the solids on or within itself. The degree of filtration obtained is proportional to the porosity of the filtering medium; the lower the porosity, the smaller the size of particulate matter removed.

5. Adsorption

Adsorbtion is a surface phenomenon whereby impurities in the liquid phase are removed from solution or dispersion by transfer to a physical site on the surface of the adsorbent material. Two typical applications of adsorbtion are removal of organics by activated carbon and selective removal of ions by ion exchange resin.

B. Physical Treatment Processes

1. Gravity separators
   a. API separators

   Vessels constructed in accordance with designs published by the American Petroleum Institute to effect the separation of free (non-emulsified) oil from water and solids. They are used at nearly all refineries and many other industrial plants. Chemicals are typically added to the API separator influent to assist the separation process.

   b. Enhanced gravity separators

   Centrifuges and cyclones are devices in which a liquid is subjected to multiple gravity forces as a result of high speed rotation. In centrifuges the liquid enters into a rotating bowl or disk. In cyclones the liquid spins by as a result of following a flow path through the device. In either case, the components of the liquid stream are separated due to differences in specific gravity. Each component stream is removed separately.

2. Coagulation & flocculation
   a. Clarifiers

   Clarifiers are used to effect the settling and removal of particulate matter from aqueous streams. Particulate matter is coagulated, then flocculated forming heavy masses of particles which are heavier than water and settle to the bottom of the clarifier where they are mechanically removed. Clean effluent water is typically discharged by overflow from the clarifier.

   b. Air flotation devices

   Air or gas flotation devices function in the same basic manner as clarifiers, with one exception. This being that particulate matter is floated to the top of the device where it is skimmed from the surface of the liquid. In order to enhance the flotation of particulate matter, air or gas is dissolved or injected under pressure into the influent water stream. When this pressure is released in the flotation device, myriads of small bubbles of air or gas are liberated, assisting the particulate matter in floating to the surface.

3. Emulsion & reverse emulsion breaking

   Many emulsions and reverse emulsions can be completely resolved with just the addition of heat. Heating may be performed at atmospheric pressure in a tank fitted with steam coils or a heating jacket. Some plants will apply heat in a pressure vessel. In either case, the object is to utilize the heat energy

to overcome the interfacial tension between the phases and to effect their separation.
Some emulsions and reverse emulsions can be completely resolved by the addition of the proper demulsifying agents to the process stream under ambient conditions.

More typically, it is necessary to apply both demulsifiers and heat to a process stream in order to effect complete resolution of the emulsion or reverse emulsion. Proper selection of the method of treatment of emulsions and reverse emulsions is based primarily on trial and error and past experience.

4. Filtration
   a. Pressure filters
      (1) Replaceable, cleanable media
      Sand filters, multi-media filters and element type filters which can be cleaned on site
      (2) Fixed Media
      Filter presses and similar types.
      (3) Disposable Media
      Disposable cartridges, bags, screens, etc.
5. Adsorption
   a. Ion exchange
   Ion exchange is often used to remove a specific hazardous ion or ions from solution and exchange it with a nonhazardous ion. All ion exchange compounds are complicated organic resins whose properties can be specifically tailored for a particular application. Ion exchange resins have great porosity and thus large surface area per unit of volume. Their entire surface is covered with active ion-exchange sites. Most ion exchange resins can be regenerated by the application of certain chemical compounds. The hazardous materials are thus concentrated in the spent regenerant where they can be more easily processed.
   b. Activated carbon
   Activated carbon is specially processed charcoal which has a surface affinity for many organic and other compounds. These compounds are attracted to the surface of the activated carbon where they become bound by loose electrostatic bonds. Other materials such as silica gel, activated alumina, fullers earth and certain clays also exhibit high adsorptive properties. The degree of adsorption is influenced by the type of adsorbent used, contact time and temperature of the fluid stream.

IV. Implications Of Current And Anticipated Regulatory Structure

The State of California began regulating used oil in January of 1979. Regulatory responsibility was assumed by the Waste Management Board. This date coincided with the requirement for licensing of used oil haulers. Major changes were implemented with the passage of Senate Bill 86 which took effect in January of 1987. S.B. 86 referenced used oil to Title 22 of the California Administrative Code. The next major change will occur on June 1, 1988 when a ban on untreated hydrocarbons being discharged to a landfill will take effect.

V. Factors To Be Considered In Selecting A Physical Treatment Technolog

A. In-Plant

1. Local-state-federal regulations governing proposed site
2. Proximity of disposal sites (Class I/II/III)
3. Physical constraints of proposed site
4. Types of contaminants
5. Results of "treatability" studies
6. Economics of various technologies
7. Availability of trained plant operations personnel
8. Availability of vendors and/or technical support personnel

B. Permitted Recyclers

1. Is facility fully permitted by all agencies?
2. Can facility process your waste stream?
3. Is transportation to recycler available and reasonable in cost?
4. Does recycler have a proven track record of compliance with regulations and successful processing of wastes similar to yours?
5. Is recycler capable of working with you to minimize the volume of your waste stream and minimize the cost of processing it?
6. Can recycler determine when waste streams are not suitable for recycling and thus eliminate contamination of recyclable streams with non-recyclable streams?

VI. Estimated quantities of used oil & waste oil processed in Kern Co.

A. Currently

The Kern County Health Department has made these estimates for the calendar year 1986:

Waste Oil : Generated: 3080 tons
Imported : 6892 tons
Total : 9972 tons

Oil Sludge: Generated: 1653 tons
Imported : 6141 tons
Total : 7794 tons

Total Of Waste Oil & Oil Sludge: 17766 tons

B. Projected

Data is not yet available for 1987 or 1988. The impact of recently enacted legislation as well as that legislation which will take effect this year is uncertain at best. It is anticipated, however, that quantities of used oil and waste oil processed in Kern County will increase significantly over 1986 levels.

VII. Description Of Facilities At Gibson Oil & Refining Co., Inc.

A. Segregation
All incoming waste streams are tested for suitability for recycling. Those streams meeting acceptability and treatability standards are segregated according to oil and/or solids content. This is done to facilitate the proper treatment of each type of waste stream.

B. Settling
Natural separation of water, oil and solids occurs in on-site storage tanks. Typically, three streams are taken from the storage tanks at various levels within the tank. These streams are (1) Primarily oil and/or solids, (2) Primarily water with little oil or solids and (3) Primarily water with high solids content.

C. Chemical Treatment
Initial chemical treatment of each process stream takes place at this point. Chemical treatment is a batch process which is dependent upon the properties of the particular stream. Treatment may be as simple as pH adjustment. Then again, it may involve a lengthy series of steps utilizing several chemical products and treatment procedures.

D. Heat
Most oil/water separations involve the use of heat. Several methods of applying heat to a process stream are available. These include tank steam coils, a process heater and a "heater-treater".

E. Enhanced gravity settling
Two methods of enhanced gravity settling are used. One is a high speed centrifuge for the removal of solids from water streams. The other is a "cyclonic" coalescer for the removal of oil from water streams.

F. Filtration

Filtration is used as the final polishing step for both water and oil streams. Different types of filtration equipment is used depending upon the application. These include disposable cartridges; rotary drum vacuum precoat; and fixed media, self-cleaning "absolute" filters.

VIII. CONCLUSIONS

A. In selecting a physical treatment process for the treatment of used oil or waste oil, the characteristics of the stream to be processed are critical.

B. Commercial recycling of used oil or waste oil streams offers the benefits of lower costs to the generator, reduced loads on the few remaining disposal sites and the reuse of increasingly scarce resources: water and oil.

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OVERVIEW OF EMERGING OILY WASTE TREATMENT TECHNOLOGIES

Bob Long, Long Consulting

Background

The main characteristic of an emerging technology in our modern society is not so much its complete technical novelty as it is the timeliness of its application. The rapidly changing regulations, the decreasing number of available options, and the rapidly rising costs of disposal of hazardous wastes have made viable some technologies which were formerly thought to be too expensive or too sensitive for general large-scale use. These technologies have usually had their origins in the treatment of specialized wastes, as in the case of wet oxidation, or in the preparation of potable water, as in membrane processes and adsorption on activated carbon. As the quality required of aqueous effluents becomes closer to that of potable water, it is not surprising that processes capable of producing such effluents are the emerging technologies. Furthermore, future technologies must minimize, or preferably eliminate, the production of by-product streams (such as oily sludges) which must be disposed of as hazardous waste. This means that successful technologies should either completely destroy hazardous substances or, alternatively, render them harmless.

Review of Established Technologies

The established technology for treating oily waste consists of one or usually several of a group of unit operations common to aqueous waste treating. The goal has historically been to recover the oil, prepare the water for disposal to a conventional sewage plant, and recover solids for disposal to a land-fill. The number of unit operations needed to achieve this depends on the complexity of the oily waste and the ultimate disposal of the oil and the water. These unit operations are summarized in Slides 1 to 4 along with brief comments on their advantages and disadvantages. A typical simple treating process made up of gravity settling, chemical treating, and filtration is shown in Slide 5. This slide illustrates two major reasons for the need for improved technology. First, large amounts of oily sludge are generated by the treatment process and second, dissolved organic toxic materials may still be left behind in the effluent water, to say nothing about the cost of the chemicals.

Driving Forces for Innovative Technologies

As mentioned in the Background above, the main driving forces for the need for innovative oily waste treatment technology are (Slide 6) environmental, regulatory, and economic. Most established technologies for treating oily waste generate an oily solids or sludge by-product which must be disposed of as a hazardous waste. This makes the treating process a hazardous waste generator with all the attendant liability and permitting requirements that go with this classification. Furthermore, the number of options for disposal of this material has been greatly decreased since it can no longer be land-filled.

The ideal technology for oily wastes is one which recovers most of the oil as a recyclable product, cleans up the water to a purity where it can be recycled disposed of to a municipal sewage plant, or disposed of to a waterway, does not generate any chemical or oily sludge, and is economical.

Slide 7 shows the priority order for new technology. Source reduction and recycling have been discussed in other blocks of this Seminar. Our speakers this afternoon will be discussing primarily treatment, with emphasis on the elimination of the hazardous waste by destroying it in aqueous solution and the possible de-listing of hazardous sludges by removing waste oil and drying the solids.

Some Promising Emerging Process Technologies

The emerging technologies which will be discussed by other speakers this afternoon fall into two basic categories, wet oxidation of oily waste and extractive clean-up of oily sludge. Wet oxidation is basically a low temperature incineration process which can be operated either subcritically or supercritically with regard to the water. Furthermore, it can be operated either above ground in process vessels or below ground in a downhole reactor. The main advantage of supercritical over subcritical operation is that higher temperatures can be used and either shorter contact times or higher conversions can be achieved. The price for this benefit is the higher required pressure of operation and increased capital costs. The optimum is a balance between size of the plant, clean-up levels which must be achieved, and the nature of the waste.

Slide 8 shows the processes which will be covered by the other speakers today. The supercritical wet oxidation processes will be the Modar Process for aboveground operation and the Oxidyne Process for belowground. The subcritical oxidation processes are the Zimpro Process for aboveground operation, which will also be discussed today, and the Vertech Process which is a downhole process much like the Oxidyne Process, except for being subcritical, and is included for completeness even though time does not permit including a detailed discussion of it on the program.

In addition to the discussions of the wet oxidation processes, we are also going to hear about a novel approach to cleaning up oily sludge which shows promise as an emerging technology. This is the Basic Extraction Sludge Treatment technology or B.E.S.T. process which has potential for making hazardous sludges innocuous and takes advantage of some very unusual physical chemistry of aqueous solutions.

In addition to the emerging technologies which will be discussed in some detail this afternoon, there are several more technologies on the horizon which should be mentioned. These are shown in Slide 9. The supercritical extraction process makes use of carbon dioxide as a solvent and is proposed for both removal of organics from water and for cleaning up oily sludges. The special benefit of using carbon dioxide is that its critical temperature is quite low (30 degrees C.), the critical pressure (1200 psi) is much lower than that of water, and traces of residual solvent in the water are not a toxicity problem. Extraction with supercritical carbon dioxide has been commercialized in the food industry, for example, to de-caffeinate coffee, but its application to waste treating is new and must still pass the tests of reliability, effectiveness, and economics on a large scale.

Activated carbon adsorption is a relatively unique process in its ability to collect toxic organics from solutions in water. Because the impurities are only on the surface of the carbon, the adsorbent bed has a relatively limited capacity for dissolved organics and can only be used effectively on relatively dilute streams. Furthermore, the carbon must be regenerated because the disposal of large amounts of solids containing toxic wastes to landfills is illegal in California and expensive if shipped to other States. Historically, regeneration has usually been done by steaming or thermal methods which were frequently incomplete and still eventually required some landfill disposal. Recently supercritical extraction of the carbon with carbon dioxide and wet oxidation of the carbon have been suggested as regeneration techniques.

A new process for using activated carbon adds powdered carbon to the reactor in a biological system and takes advantage of the better adsorption characteristics of powdered carbon over granular carbon as well as the longer contact time available in a biological plant. In addition, the sludge from the biological processes along with the spent carbon adsorbent are sent to a wet oxidation process which regenerates the carbon and destroys the biological sludge, eliminating almost all the requirement for landfilling. The biological and adsorption processes are synergistic giving better cleanup together than when used consecutively.

The final emerging process technology I will mention is ultrafiltration (Slide 10), which has in the past been considered incapable of handling large volumes and also too expensive for general use. This technology is an outgrowth of the reverse osmosis process for removing salts from water but uses a larger pore membrane and doesn't require as great a pressure drop to drive water through the membrane. It generally operates at below 50 psi upstream pressure and effectively removes both soluble and emulsified oils from aqueous streams without the addition of chemicals. Volume reductions of up to 97% can be achieved for a wide variety of waste streams with continuous operation. The membranes need to be cleaned periodically and large volumes of oil and grease are impractical to handle. However, even though the initial cost is quite high, total operating cost studies have shown that for a flow rate of 1000 gallons per day ultrafiltration is actually less expensive than chemical treating in a comparable size plant. Its simplicity of operation would make this technology ideal for smaller plants where the quality of the aqueous ultrafiltrate is such that it could be sent directly to the sewer if only the costs of ultrafiltration can be made competitive on a smaller scale. This might be possible if the cost of membrane manufacture can be reduced due to much larger demand.

Emerging Management Practice

While not a new process technology, a new wrinkle in handling oily wastes is being pioneered in New Jersey by Dupont (Slide 11). This consists of using the excess capacity in a privately owned industrial water treating plant to treat wastes brought to it by other generators. Dupont has a centralized waste treatment facility in New Jersey that accepts contaminated oily wastewater from outside sources to utilize the excess capacity of its chemical treatment complex. It is not the process technology that is novel, because this same treating technology exists at many sites in California, but the idea of a private company generating internal profits and at the same time helping with an environmental problem by using more completely facilities for which it has already paid. This idea could also be used in California by companies which may already own or are planning to build their own wastewater treating facilities.

Slide 1

SUMMARY OF ESTABLISHED UNIT OPERATIONS

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
GRAVITY SETTLING	- ECONOMICAL - SIMPLE	- SLOW - POOR FOR EMULSIONS - LEAVES SOLUBLE OILS - LOW EFFICIENCY
FILTRATION	- BROADLY APPLICABLE - WIDE COST RANGE - EQUIPMENT AVAILABLE - HANDLES HIGH SOLIDS	- LABOR INTENSIVE - REQUIRES ENERGY - NEEDS BACKWASHING - EASILY BOUND
MAGNETIC	- FERROUS MATERIALS SELECTIVELY	- ONLY REMOVES FERROUS

Slide 2

SUMMARY OF ESTABLISHED UNIT OPERATIONS......CONTINUED

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
CENTRIFUGATION	- LARGE VOLUMES - FAST WAY TO FREE OILS AND SEPARATE SOLIDS - GOOD PRETREATMENT FOR EMULSION BREAKING	- HIGH INITIAL COST - ENERGY INTENSIVE - DIFFICULT CLEAN-OUT
HYDROCLONES	- LOW COST - HANDLES LARGE VOLUME - EFFECTIVE FOR SOLIDS - GOOD PRETREAT FOR EMULSION BREAKING	- REJECTS SOME LIQUID WITH SOLIDS - NO GOOD FOR SOLUBLE OR EMULSIFIED OILS
COALESCING PLATE FILTERS	- EFFICIENT - HANDLES HIGH VOLUMES - LOW ENERGY REQUIRED - GOOD FOR MECHANICALLY EMULSIFIED OILS	- HIGH SOLIDS FOULING - POTENTIAL BIOLOGICAL FOULING - COSTS DEPEND ON FOULING

Slide 3

SUMMARY OF ESTABLISHED UNIT OPERATIONS......CONTINUED

TECHNOLOGY	ADVANTAGES	**DISADVANTAGES**
SKIMMING	- LOW COST - MANY OPTIONS - COST EFFECTIVE FOR TRAMP OILS OR FREE FLOATING OILS	**- NOT EFFECTIVE ON EMULSIONS OR SOLUBLE OILS**
AERATION	- RELIABLE, EASY OPERATION - HANDLES HIGH SOLIDS - EFFECTIVE OVER RANGE OF LOADING	**- REQUIRES CHEMICALS** **- SLUDGE DISPOSAL**
CHEMICAL TREATMENT	- SIMPLE SCALE-UP - HANDLES HIGH SOLIDS - BREAKS SOLUBLE OIL EMULSIONS	**- LOT OF SLUDGE MADE** **- OFTEN NOT COST EFFECTIVE**

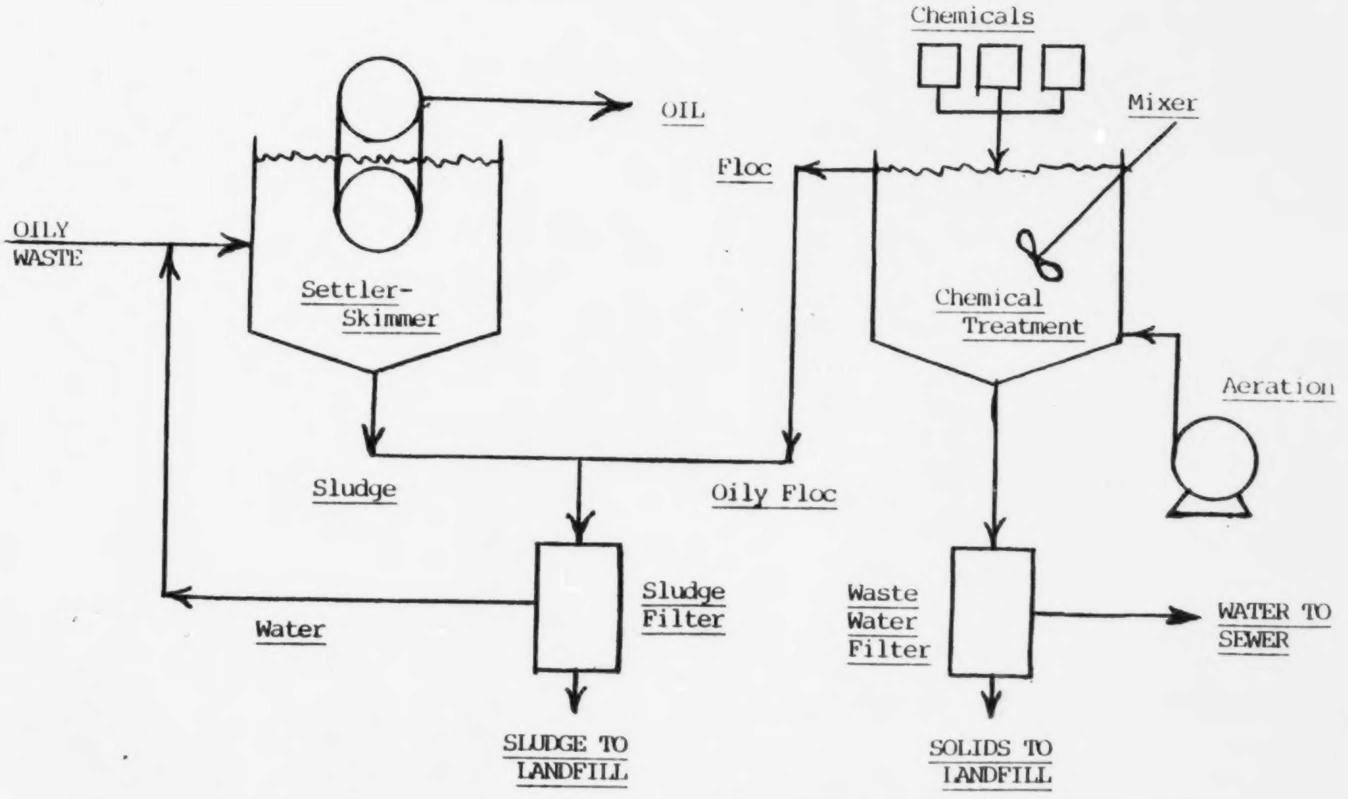
Slide 4

SUMMARY OF ESTABLISHED UNIT OPERATIONS......CONTINUED

TECHNOLOGY	ADVANTAGES	**DISADVANTAGES**
ULTRAFILTRATION	- WIDE pH RANGE - NO CHEMICALS - SEPARATES SOLUBLE AND INSOLUBLE OILS - HIGH VOLUME (97%) REDUCTION - OPERATION TO 120 F. - CONTINUOUS OPERATION WITH LITTLE ATTENTION - BROADLY APPLICABLE	**- HIGH INITIAL COST** **- ENERGY INTENSIVE** **- LOW FLUX RATES** **- MEMBRANE FOULING POSSIBLE** **- NOT PRACTICAL FOR LARGE VOLUMES OF OIL**
CARBON ADSORPTION	- REMOVES SOLUBLE OILS - FILTERS OUT VERY FINE PARTICLES	**- EXPENSIVE, REQUIRES EXTENSIVE PRETREAT** **- ENERGY INTENSIVE** **- NEEDS REGENERATION**
BIOLOGICAL TREATMENT	- REMOVES SOLUBLE OIL - HIGH TOLERANCE FOR OIL AND GREASE	**- SOLIDS CARRYOVER** **- PRONE TO UPSET** **- PRETREATMENT NEEDED**

Slide 5

SIMPLE OILY WASTE TREATING PLANT


Chemicals
OIL
Mixer
Floc
OILY WASTE
Settler-Skimmer
Chemical Treatment
Aeration
Sludge
Oily Floc
Sludge Filter
Water
Waste Water Filter
WATER TO SEWER
SLUDGE TO LANDFILL
SOLIDS TO LANDFILL

Slide 6

DRIVING FORCES FOR INNOVATION

- ENVIRONMENTAL FORCES
  - INCREASED RECOGNITION OF HAZARDS
    - + LEAKAGE IN LANDFILLS
    - + PERSISTENCE OF CERTAIN ORGANICS
  - EXPANDED LIST OF TOXIC ORGANICS
    - + IMPROVED DETECTION
- REGULATORY FORCES
  - LAWS AGAINST PAST PRACTICES
    - + NO DUMPING OF OILY SLUDGE
    - + PROHIBITION OF ROAD OILING
  - NEW LAWS
    - + WATER QUALITY REQUIREMENTS
    - + EMPHASIS ON RECYCLING
- ECONOMIC FORCES
  - HIGHER COST OF COMPLYING WITH NEW LAWS
    - + LIABILITY INSURANCE COSTS
    - + PERMITTING COSTS
  - INCREASED COST OF DISPOSAL
    - + LONGER HAULING DISTANCES
    - + HIGHER LANDFILL COSTS
    - + HIGHER TREATING CHARGES

Slide 7

PRIORITY ORDER FOR NEW TECHNOLOGY

- SOURCE REDUCTION
- RECYCLING
- TREATMENT FOR DISPOSAL

Slide 8

TOPICS ON TODAYS PROGRAM

- WET OXIDATION PROCESSES
  - SUPERCRITICAL CONDITIONS
    - + ABOVE GROUND (MODAR PROCESS)
    - + BELOW GROUND OR DOWNHOLE (OXIDYNE PROCESS)
  - SUBCRITICAL CONDITIONS
    - + ABOVE GROUND (ZIMPRO/PASSAVANT PROCESS)
    - + BELOW GROUND OR DOWNHOLE (VERTECH PROCESS)
- SLUDGE TREATMENT PROCESS
  - EXTRACTION WITH AMINE/WATER SOLUTION (B.E.S.T. PROCESS)

Slide 9

OTHER EMERGING TECHNOLOGIES

- SUPERCRITICAL EXTRACTION WITH CARBON DIOXIDE (SCF CORP., ILLINOIS WATER TREATING)
  - CLEANING UP OILY SLUDGES
  - RECOVERY OF ORGANICS FROM AQUEOUS SOLUTION
  - OPERATES NEAR AMBIENT TEMPERATURE
  - HAS BEEN COMMERCIALIZED IN THE FOOD INDUSTRY
- CARBON ADSORPTION (ENVIR. SYSTEMS CORP)
  - BASIC OPERATION IS OLD
  - PROBLEMS OF REGENERATION AND DISPOSAL ARE THREATENING PAST PRACTICES
  - NEW PROCESS USES POWDERED CARBON IN BIOLOGICAL SYSTEM
  - NEW OPTIONS FOR REGENERATION
    - + SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF CARBON
    - + WET OXIDATION

Slide 10

OTHER EMERGING TECHNOLOGIES......CONTINUED

- MEMBRANE PROCESSES

  - REVERSE OSMOSIS
    - REMOVES DISSOLVED SALTS IN OILS
    - MAKES VERY CLEAN EFFLUENT
    - EXPENSIVE

  - ULTRAFILTRATION
    - LESS EXPENSIVE
    - FITS 200 TO 2000 GAL PER DAY SIZE
    - LESS SELECTIVE THAN REVERSE OSMOSIS
    - MAY BE AMENABLE TO COST REDUCTION
    - PROVEN TECHNOLOGY FOR METALWORKING FLUIDS

Slide 11

A NEW MANAGEMENT WRINKLE

- USE OF PRIVATELY OWNED EXCESS TREATING CAPACITY

  - DUPONT PIONEERING IN N.J.
    - ACCEPTS OILY WASTE FROM OUTSIDE SOURCES
    - CAN MAKE A PROFIT FROM EXISTING CAPACITY
    - HELPS SOLVE AN ENVIRONMENTAL PROBLEM

  - OTHER COMPANIES SHOWING INTEREST
    - SHOULD BE CONSIDERED BY COMPANIES OWNING OR PLANNING TO BUILD LARGE WATER TREATING PLANTS

SUPERCRITICAL FLUID TECHNOLOGY IN HAZARDOUS WASTE TREATMENT[*]

Michael Modell
Modell Development Corporation
Framingham, MA 01701

ABSTRACT

This paper describes theory and applications of supercritical fluid technology in the physical and chemical treatment of hazardous and toxic wastes. The background section provides a brief description of the supercritical fluid properties of interest. Two quite different types of applications are discussed: (i) extraction of organics with supercritical carbon dioxide from aqueous wastes, spent activated carbon and contaminated soils and (ii) oxidation of organics in supercritical water.

Supercritical fluids (SCFs) have been receiving much attention as potential extracting agents and media for chemical reactions. This interest stems from an unusual combination of thermodynamic and mass transport properties: solubilities of nonvolatile solutes in SCFs can be varied from moderately high to very low by relatively small changes in temperature and pressure while diffusivities are significantly higher than those of the same solutes in liquid solvents. The variability of solubility provides the basis for extraction methodology. The media to be treated (e.g., liquid or solid waste) is extracted with the SCF under conditions of high solubility; the temperature and/or pressure of the extract is then altered to reduce the solubility, thereby creating a second phase which is solute-rich; the phases are separated; the SCF solvent phase is recycled and brought back to the conditions of high solubility while the solute is recovered as concentrate.

As applied to hazardous waste treatment, SCF extraction may be considered where toxic contaminants are present in low to moderate concentrations in a nontoxic, nonhazardous medium. Removal of toxic organics from aqueous wastes is one application which has recently undergone successful piloting and the first commercial unit is under construction. A second application currently in research is extraction of toxic organics from soils. Preliminary economic estimates presented herein suggest that soil decontamination by SCF might represent a breakthrough. Data, flowsheets and economics will be described, to the extent that they have been made publicly available.

As a medium for chemical reactions, supercritical water (SCW) is being used for the oxidation of organics. Above the critical temperature (374°C) and pressure (22 MPa), water is an excellent solvent for both organic matter and gases (e.g., oxygen, nitrogen, carbon dioxide). Dissolving waste and air or oxygen in SCW leads to a homogenous phase in which oxidation is rapid. At 400 to 450°C, the kinetics are such that 99 to 99.9% conversion (to carbon dioxide and carbon monoxide) can be achieved within 5 min; at 600 to 650°C, 99.9999% can be achieved in less than 1 min.

There are two applications of SCW oxidation under development: (i) a surface treatment process for oxidation of organic wastes or moderately concentrated aqueous wastes; and (ii) a downhole process for the oxidation of organics in dilute aqueous wastes. Data, flowsheets and economics of these two applications will be presented, to the extent that they have been made publicly available.

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INTRODUCTION

Over the past ten years, supercritical fluids have received considerable attention as potential extracting agents and media for chemical reactions (see, e.g., McHugh and Krukonis [1] and Paulaitas, *et al*. [2,3]. Most of the activity has been research and exploratory development; very few processes have reached commercial exploitation. Some notable exceptions are propane deasphalting, tertiary oil recovery with carbon dioxide, decaffeination of coffee with carbon dioxide and hydrothermal manufacture of quartz.

Two types of applications are of interest in hazardous waste treatment: extraction of contaminants from water and solids, and oxidation of organic contaminants from aqueous solutions and concentrates. A list of candidate materials is given in Table 1, along with critical temperatures, pressures and densities. Aliphatic and olefinic hydrocarbons are potentially attractive SCF solvents because they are relatively inexpensive and their critical pressures are relatively low. However, from the point of view of potential toxicity of residual solvent, their use in environmental applications is questionable. If we focus on environmental acceptability as well as low material cost, then we are left with only two fluids of interest: carbon dioxide and water. Note that both have relatively high critical pressures, which is a negative factor when we consider capital cost of equipment.

The applications of SCF technology discussed herein are listed in Table 2. The first three entries involve supercritical carbon dioxide for removal of organics by extraction and/or desorption. The underlying phenomena involve solubility and mass transfer characteristics of solutes in SCF solvents. The last two entries concern the oxidation of organics in supercritical water (SCW) and are based upon the kinetics of oxidation in addition to solubility relationships.

The scientific bases of the underlying phenomena are treated in two parts. The section on properties of supercritical carbon dioxide is applicable to SCF extraction processes and supercritical fluids in general. Water is a notable exception to those generalities and, therefore, the properties of supercritical water are treated in a separate subsection.

Following the description of underlying phenomena, each of the applications listed in Table 2 is discussed. Flowsheets are presented and projected economics of commercial operation are given. Where costs have been published by the organizations developing the processes, they are provided herein. Where costs were unavailable in the open literature, the author has taken the liberty of providing his own estimates. The purpose of including such estimates is to provide the reader with some idea of the *magnitude* of costs associated with each of the processes. In spite of the fact that the author has been associated with the development of some of these processes, the estimates and extrapolations contained herein are not necessarily made with knowledge of the current state of technology development and do not necessarily represent the views of the organizations that are offering or will offer such processes commercially. For more accurate and current commercial and technical information, the reader should contact the organizations listed as sponsors in Table 2.

SUPERCRITICAL FLUID EXTRACTION

1. Properties of Supercritical Fluid Solvents

The supercritical fluid region can best be visualized with the aid of a reduced pressure-density diagram, shown in Fig. 1. The dashed curve is the

TABLE 1

CRITICAL CONSTANTS OF SOME COMMON FLUIDS

	Critical Constants		
	Temp. (C)	Pres. (MPa)	Dens. (g/cm^3)
Ethylene	9.9	5.12	0.23
Chlorotrifluoromethane	28.8	3.87	0.58
Carbon dioxide	31.0	7.38	0.47
Ethane	32.2	4.88	0.20
Propylene	91.9	4.60	0.23
Propane	96.7	4.25	0.22
Dichlorotrifluoromethane	111.7	3.99	0.56
Ammonia	132.3	11.27	0.24
n-Butane	152.0	3.80	0.23
n-Pentane	196.6	3.37	0.23
Isopropyl alcohol	235.3	4.76	0.27
Methanol	240.3	7.99	0.27
Ethanol	243.4	6.38	0.28
Benzene	288.9	4.89	0.30
Water	374.2	22.12	0.32

TABLE 2

APPLICATIONS OF SUPERCRITICAL FLUIDS IN HAZARDOUS WASTE TREATMENT

Methodology	Application	Fluid	Conditions	Sponsor
Desorption	Regeneration of adsorbents	Carbon dioxide	80-100°C, 8-15 MPa	Illinois Water Treatment Co. Rockford, IL
Extraction and desorption	Decontamination of soils	Carbon dioxide with and without cosolvents	40-80°C, 7-10 MPa	Louisiana State University Baton Rouge, LA
Extraction	Removal of organics from aqueous wastes	Carbon dioxide with and without cosolvents	20-30°C, 6-8 MPa	Critical Fluid Systems, Inc. Cambridge, MA
Oxidation	Destruction of organics and removal of salts	Water	450-650°C, 25 MPa	Modar, Inc. Houston, TX
Oxidation	Downhole destruction of organics in dilute aqueous waste	Water	300-450°C, 25-30 MPa	Oxidyne, Inc. Dallas, TX

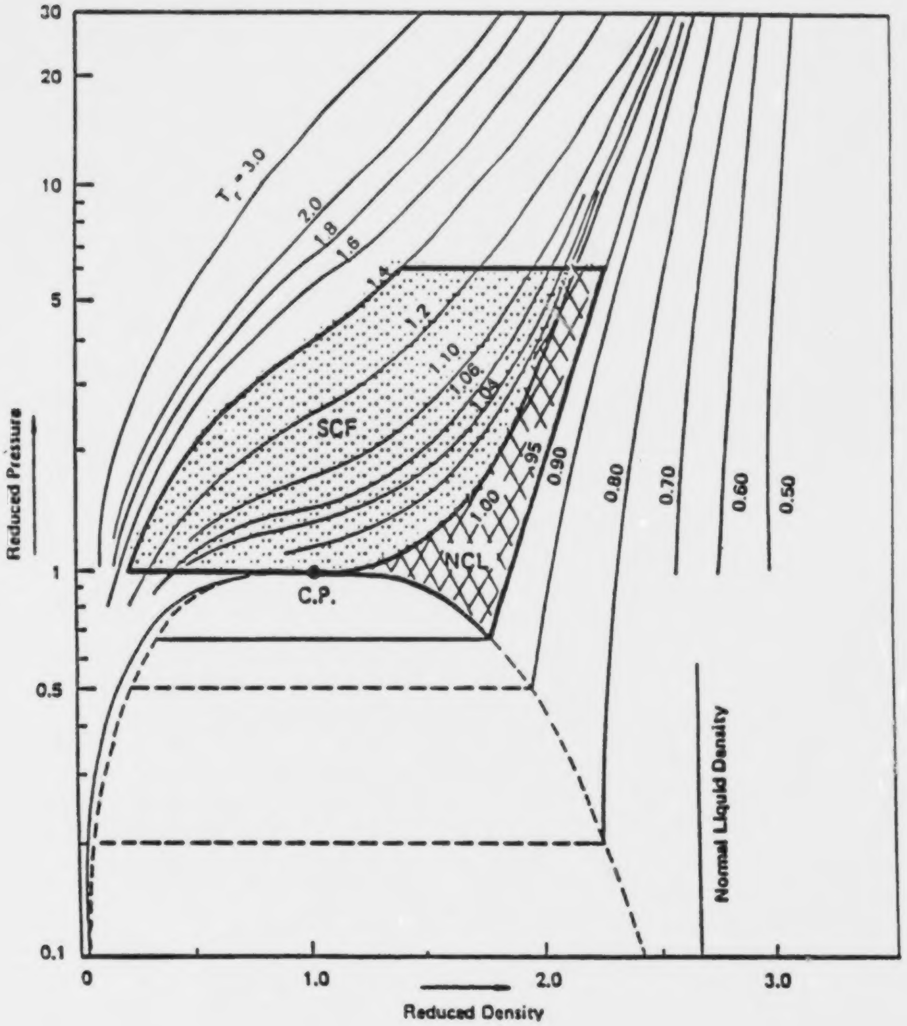


FIGURE 1.

REDUCED PRESSURE-DENSITY DIAGRAM. Supercritical fluid (scf) and near-critical liquid (ncl) regions, as indicated locus of liquid-vapor equilibria, which terminates at the critical point (C.P.). Note that the critical density is about 40% of that of the normal liquid.

The range of conditions of interest is reduced temperatures of 0.95 to 1.4 and reduced pressures of 1 to 6. As shown in Fig. 1, the region above $T_r=1$ is a supercritical fluid; the region below $T_r=1$ is referred to as a near critical liquid (NCL). Within these regions, there are conditions which are optimal for extraction: densities high enough to provide liquid-like solubilities, yet low enough so that diffusivities are appreciably higher than those of normal liquids [4].

The extraction cycle can be illustrated by a solubility "map," as shown in Fig. 2 for naphthalene in CO_2 [4,5]. The dashed line is the solubility of solid naphthalene in coexisting liquid and vapor CO_2. A vertical tie line is shown for 25°C. The critical point indicated in Fig. 2 is actually the critical end point for the naphthalene-carbon dioxide mixture. It occurs near the critical point of CO_2 because the concentration of naphthalene is small.

Outside of the liquid-vapor envelope, the solubilities shown in Fig. 2 are isobars for solid naphthalene in equilibrium with a supercritical fluid mixture. The solubilities are directly related to fluid density. At temperatures slightly above the critical (32 to 50°C), the solubility drops dramatically with decreasing pressure because density decreases significantly with small decrease in pressure (see Fig. 1).

As pressure increases, it requires a higher temperature to obtain the sharp drop in density. At 15 to 30 MPa, the solubility increases with increasing temperature in the conventional manner (i.e., solute activity increases with higher temperature) because the fluid density does not decrease appreciably until the temperature is higher than 50°C.

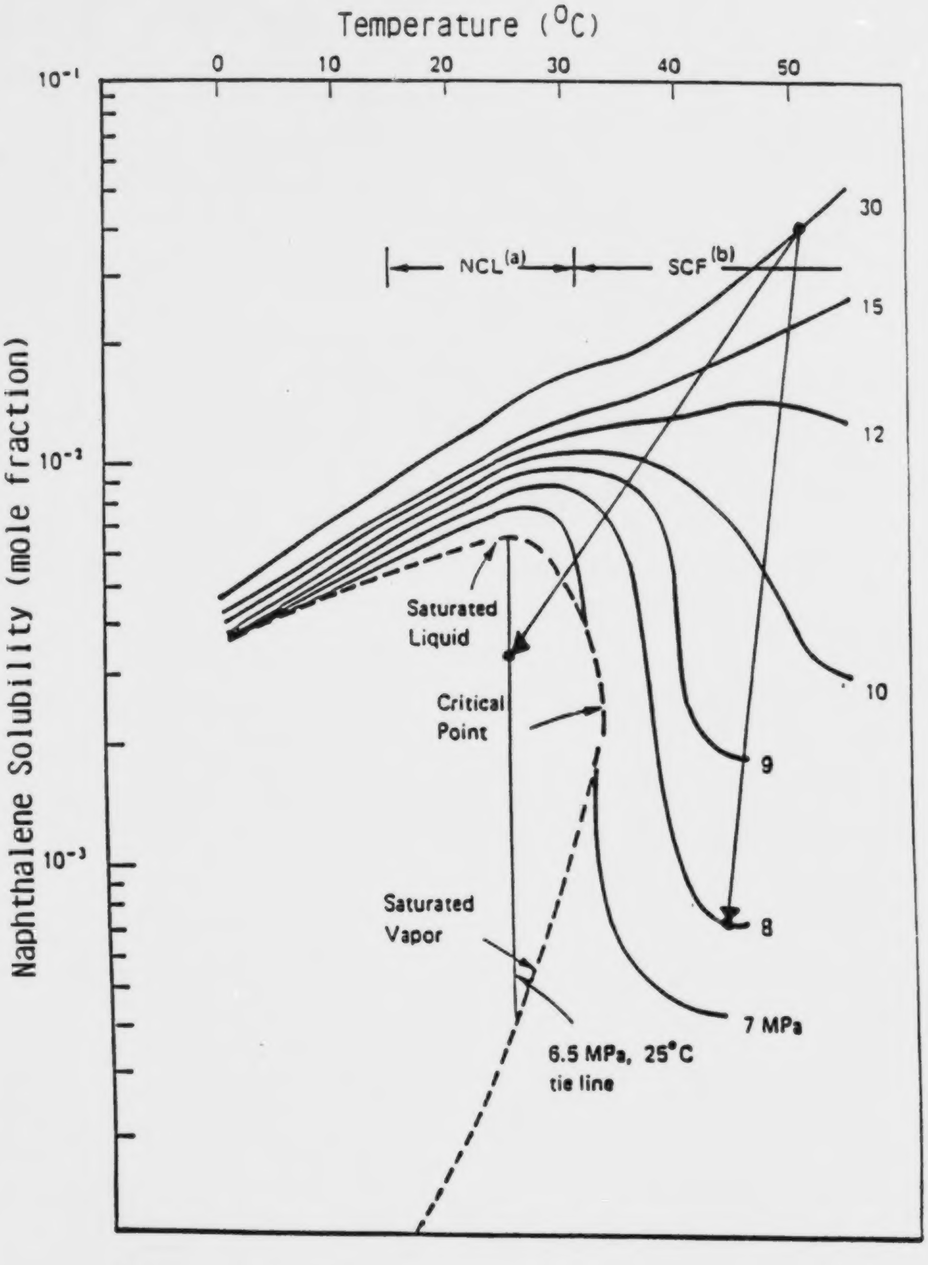
An extraction cycle consists of a condition of high solubility, where extraction takes place, and a condition of low solubility, where solute is removed from the solvent. After separation, the solvent is returned to the first condition to complete the cycle.

Two extraction cycles are indicated on Fig. 2. Both start with extraction under conditions of high solubility at high pressure (e.g., 50°C, 30 MPa). In one cycle, pressure would be decreased to 8 MPa and the temperature adjusted to 45°C to provide for a condition of low solubility. In the second cycle, the mixture would be brought to subcritical conditions where a single stage or multistage distillation would be used to separate solute and solvent.

Fig. 2 illustrates general variations of solubility with temperature and pressure. However, the absolute values of solubilities can vary widely from one substance to another and the economics of extraction depend upon these absolute values. For CO_2, there is a large body of data for solubilities in liquid CO_2 that can be used as a guide. Table 3 is a partial compilation of solubilities of organics in liquid CO_2 at 25°C and 6.6 MPa [6]. Each of these solubilities represents a single data point on a solubility map. For example, from Table 3, the solubility of naphthalene in liquid CO_2 at 25°C is 2 wt%. In Fig. 2, the corresponding point on the saturated liquid curve at 25°C is 0.62 mole-% or about 2 wt%. Thus, the data of Table 3 can be used as a guide for estimating the magnitude of solubility in the critical region. It should be noted that nearly half of the entries in Table 3 are completely miscible with NCL CO_2. The naphthalene solubility behavior discussed above is representative of the less soluble organics in CO_2.

FIGURE 2.

SOLUBILITY MAP OF NAPHTHALENE IN SCF AND NCL CO_2



(a) NCL = Near Critical Liquid
(b) SCF = Super Critical Fluid

TABLE 3. SOLUBILITIES OF ORGANIC COMPOUNDS IN LIQUID CO_2 AT 25°C AND 6.6 MPa [6]
(Solubilities in weight-percent; M = completely miscible)

Paraffins	
Cyclohexane	M
n-Dodecane	M
Ethane	M
n-Heptane	M
n-Hexadecane	8
Methylcyclohexane	M
n-Octadecane (mp 28 C)	3
Paraffin wax (mp 52 C)	1
Propane	M
n-Tetradecane	16

Olefins	
1-Decene	M
1-Octadecene	10
Propylene	M

Aromatics	
Benzene	M
Biphenyl (mp 71 C)	2
Chlorbenzene	M
a-Chloronaphthalene	1
p-Dichlorobenzene (mp 53 C)	M
p-Dimethoxybenzene (mp 53 C)	M
2-Methoxybiphenyl (mp 29 C)	5
B-Methylnaphthalene (mp 35 C)	9
Naphthalene (mp 52 C)	2
Nitrobenzene	M
o-Nitrocholorobenzene (mp 32)	21
a-Nitronaphthalene (mp 58 C)	1
o-Nitrotoluene	M
p-Nitrotoluene (mp 51 C)	20
Tetrahydronaphthalene	12
Toluene	M

Alcohols	
Benzyl alcohol	8
B-Chloroethanol	10
Cinnamyl alcohol (mp 30 C)	5
Cyclohexanol	4
1-Decyl alcohol	1
2-Ethylhexanol	17
Ethyl alcohol	M
Furfuryl alcohol	4
Heptyl alcohol	6
Hexyl alcohol	M
Methyl alcohol	M

Aldehydes	
Acetaldehyde	M
Benzaldehyde	M
Cinnamaldehyde	4
1-Heptaldehyde	M
Salicylaldehyde	M
Valeraldehyde	M

Ketones	
Acetone	M
Acetophenone	M
Benzalacetone (mp 42 C)	5
Benzophenone (mp 48 C)	4
Chloroacetone	M
Cyclohexanone	M
2-Octanone	M

Ethers	
n-Butyl ether	M
B,B'-Dicholroethyl ether	M
Phenyl ether (mp 28 C)	8

Phenols	
o-Chlorophenol	M
p-Chlorophenol (mp 43 C)	8
o-Cresol (mp 30 C)	2
m-Cresol	4
2,4-Dichlorophenol (mp 45 C)	14
p-Ethylphenol (mp 46 C)	1
o-Nitrophenol (mp 45 C)	M
Phenol (mp 41 C)	3

Esters	
Benzyl benzoate	10
Butyl oxalate	M
Butyl phthalate	8
Butyl stearate	3
B-Chloroethyl acetate	M
Ethyl acetate	M
Ethyl benzoate	M
Ethylene diformate	M
Ethyl lactate	M
Ethyl phthalate	10
Ethyl salicylate	M
Ethyl succinate	M
B-Hydroxyethyl acetate	17
Methyl phthalate	6
Phenyl phthalate (mp 70 C)	1
Phenyl salicylate (mp 43 C)	9

Amides	
Acetamide (mp 82 C)	1
N,N-Diethylacetamide	M
N,N-Diethylformamide	M
N,N-Dimethylformamide	M
Formamide	0.5

Carboxylic Acids	
Acetic acid	M
Caproic acid	M
Caprylic acid	M
Chloroacetic acid (mp 61 C)	10
a-Chloroproprionic acid	26
Isocaproic acid	M
Lactic acid	0.5
Lauric acid	1
Oleic acid	2

Amines and Nitrogen Heterocyclics	
Aniline	3
o-Chloroaniline	5
N,N-Diethylaniline	17
N,N-Dimethylaniline	M
Diphenylamine (mp 53 C)	1
N-Ethylaniline	13
N-Ethyl-N-benzylaniline	4
N-Methylaniline	20
a-Naphthylamine (mp 52 C)	1
Phenylethanolamine	1
2,5-Dimethylpyrrole	5
Pyridine	M
o-Toluidine	7
m-Toluidine	15

Nitriles	
Acetonitrile	M
Acrylonitrile	M
Benzonitrile	M
B-Hydroxyproprionitrile	1
Phenylacetonitrile	13
Succinonitrile (mp 54.5 C)	2

Several generalities can be gleaned from Table 3: (i) for a given homologous series, solubility decreases with increasing molecular weight; (ii) increasing polarity and/or hydrophilicity tends to decrease solubility; and (iii) liquids tend to be more soluble than solutes that are solids at the temperature in question.

2. Regeneration of Activated Carbon

Regeneration of spent activated carbon from wastewater treatment is the first reported environmental application involving supercritical fluids [4,7-9]. Although the process has not yet been used on a commercial scale, it provides a basis for evaluating other applications involving desorption of solutes from solids. In particular, the economics of carbon regeneration have been used to estimate the costs for decontamination of soil with SCF CO_2.

A flowsheet for the process is shown in Fig. 3. The SCF CO_2 circulates through a recycle loop: first through a desorption vessel, where it picks up solute, then through an expander or valve to reduce pressure, and on to a heat exchanger to bring the temperature to the conditions required for solute precipitation. The solute is recovered in a separator and the solvent is brought back to the conditions required for desorption by heat exchange and recompression.

In the semi-batch mode of operation shown in Fig. 3, adsorption and desorption are carried out in different vessels. (Adsorbers are not shown in Fig. 3.) Three high-pressure vessels are used for desorption. At any one time, two vessels are offline for loading and unloading of activated carbon and carbon dioxide, while the other vessel is online undergoing desorption. In this manner, the SCF recycle loop is operated continuously.

Economic estimates for SCF CO_2 regeneration of activated carbon are given in Table 4. Two columns of annual cost estimates are given: the first, for a throughput of 1,650 ton/yr, were published by deFilippi, *et al*. [9]; the second column, for 20,000 ton/yr, were extrapolated by the author assuming fixed costs vary with the 0.6 power of throughput, variable costs are directly proportional to throughput, and labor varies as shown in the table.

At 1,650 ton/yr, the unit cost of $169/ton is not sufficiently attractive to displace thermal regeneration of carbon. However, Table 4 indicates that there are large economies of scale to be had at higher throughputs.

Extensive bench scale studies [9] showed that strongly bound adsorbates could not be removed by SCF regeneration and that, depending on the solute and carbon, from 10 to 30% of the adsorbate might fall in that category. Physically adsorbed species were removed very rapidly and completely; so rapidly, that the column approached local equilibrium behavior [10].

As long as the regenerated carbon is used to adsorb the same species in subsequent cycles, the presence of the residual adsorbate does not alter the quality of the treated effluent (although it does reduce the capacity compared to virgin carbon). On the other hand, this phenomena restricts the potential applications of the process. For example, if the solute varies from day to day, it is conceivable that a more strongly adsorbable species could displace the residual solute that is not removed during regeneration. Thus, the process is not appropriate for use in centralized regeneration facilities, which are the ones that tend to operate at high levels of throughput where the economies of scale would be most beneficial.

FIGURE 3. SUPERCRITICAL FLUID EXTRACTION OF SOLUTES FROM SOLIDS

(Source: Illinois Water Treatment Co.)

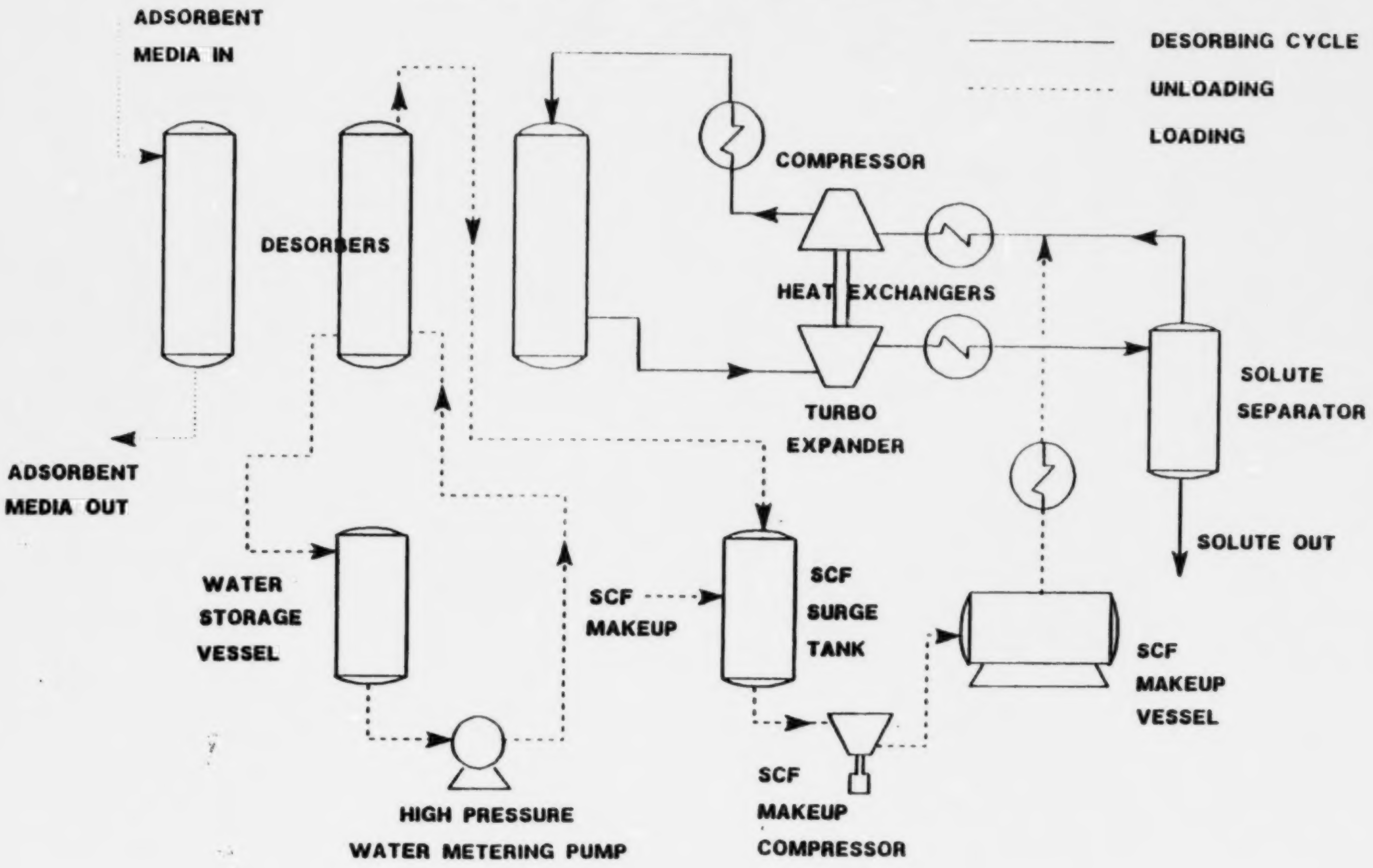

ADSORBENT MEDIA IN
DESORBERS
ADSORBENT MEDIA OUT
COMPRESSOR
HEAT EXCHANGERS
TURBO EXPANDER
DESORBING CYCLE
UNLOADING
LOADING
SOLUTE SEPARATOR
SOLUTE OUT
WATER STORAGE VESSEL
HIGH PRESSURE WATER METERING PUMP
SCF MAKEUP
SCF SURGE TANK
SCF MAKEUP COMPRESSOR
SCF MAKEUP VESSEL

TABLE 4

COST ESTIMATES FOR SUPERCRITICAL CO_2 REGENERATION OF ACTIVATED CARBON

BASIS [9]

Solute	phenol from wastewater
Desorption Temperature	120°C
Desorption Pressure	150 atm
Precipitation Temperature	45°C
Precipitation Pressure	80 atm

ESTIMATED COSTS (1978-1979 dollars)

	Annual Costs ($000)	
CAPACITY:	1,650 ton/yr	20,000 ton/yr
REFERENCE:	[9]	*
Variable Costs		
Electricity ($.03/kW-hr)	2	20
Cooling water ($.10/million gal)	15	180
Steam ($3.50/million Btu)	50	600
Make-up CO_2 ($.03/lb)	5	60
	72	860
Semivariable Costs		
Operating labor (0.5 and 2 man/shift)	40	160
Supervision (0.5 and 1 man)	13	20
Labor overhead (40% of labor & supervision)	21	70
Plant overhead (60% of labor & supervision)	31	110
	65	200
Fixed Costs		
Depreciation (10% of capital investment)	77	340
Maintenance (2% of capital investment)	15	70
Taxes & insurance (1.5% of capital investment)	11	50
	103	460
Total Annual Cost ($000)	280	1,690
Unit Cost ($/ton activated carbon)	169	84

---

* Estimates by author

3. Decontamination of Soils

The semibatch process illustrated in Fig. 3 could be applied quite generally for removal of contaminants from solids. In particular, there is interest in removing organic contaminants from soils. Knopf and co-workers at Louisiana State University have studied extraction of polychlorinated biphenyls (PCBs), DDT and toxaphene from contaminated topsoils and subsoils [11,12]. CO_2 extraction of wet subsoil (20% water) contaminated with 1,000 ppm PCBs was effective at 40°C and 10 MPa: over 90% of the solute was extracted in the order of 10 min at a space velocity of 0.07 g CO_2/g soil/s [11].

Topsoil contaminated with DDT (1,000 ppm) and toxaphene (400 ppm) could be decontaminated to about 70% of the adsorbates within 10 min, but the other 30% did not respond to longer extraction time. The authors suggested that the residual might be strongly adsorbed. In a recent publication, the same authors subsequently showed that over 95% of adsorbed DDT could be removed within 5 min at the same conditions by using a supercritical solvent mixture of 95 wt% CO_2 and 5 wt% methanol [12].

The cost of soil decontamination can be estimated, to a first approximation, by analogy to activated carbon regeneration. For the 20,000 ton/yr case given in Table 4, there are three factors which have major effect on cost: (i) the operating pressure impacts the fixed costs through the weight of vessels and the like; (ii) the supercritical fluid recirculation rate (wt of solvent/wt of solid, which is proportional to space velocity x desorption cycle time) influences the capital cost of compressor and heat exchangers as well as the operating costs, which are directly proportional to SCF recirculation rate; and (iii) the temperature of desorption, impacts the heat exchanger capital cost and the heating and cooling costs.

The temperature and pressure used for the activated carbon regeneration process (see Table 4) are both more severe than the conditions used by Knopf for soil decontamination. The space velocities and desorption cycle times are the same order of magnitude for the two applications. Thus, the costs shown in Table 4 can be viewed as conservative estimates of the cost of decontaminating soil by supercritical fluid treatment. Since 20,000 ton/yr is a throughput equivalent to a small remedial action site in the U.S. (typically 50,000 to 100,000 total tons of contaminated soil), the estimated cost of $84/ton may be viewed as an upper limit. Soil decontamination costs below $100/ton are viewed as extremely attractive; the cost of burial of contaminated soils in Class I landfills exceed $200/ton, excluding transportation, in the U.S. Thus, SCF decontamination appears to be extremely attractive and potentially represents a breakthrough if these preliminary economics can be confirmed by subsequent evaluation and development.

4. Removal of Organics from Aqueous Wastes

All organics are not highly soluble in supercritical or near critical CO_2. As a general rule, hydrophobic compounds are more soluble than hydrophilic materials (e.g., compare alcohols with paraffins or anilines with aromatics in Table 3). However, toxic compounds tend to be hydrophobic. Thus, the processing concept is to extract toxic organic contaminants from aqueous wastes and, if necessary, subsequently treat the dilute aqueous effluent by biological oxidation or activated carbon to remove the remaining organics.

Most of the research and development of this process has been done by Critical Fluid Systems (CFS), Inc. [13-16]. Several pilot plants have been built and the first commercial unit is under construction. Although the design details have not been made public, it is presumed that the commercial units will be of a design similar to that used for pilot tests, a schematic for which is given in Fig. 4 [15]. The aqueous waste is fed to an extraction column, which is under pressure and fed countercurrently with pressurized CO_2. The CO_2 is a near critical liquid if the extractor is operated at room temperature, as is the case for the process illustrated in Fig. 4. The treated aqueous effluent exits the bottom of the extractor and may require post treatment, as discussed above.

The CO_2 extract, containing organic and some water, is depressurized (to the pressure chosen for distillation) and fed to a decanter where an aqueous liquid phase may form and, if so, is removed. The CO_2 fluid phase is then passed to a distillation column where purified CO_2 vapor is removed overhead while a condensed organic phase (and possibly some water) is recovered from the reboiler. The purified CO_2 is recompressed to the extractor pressure, condensed in the reboiler and then recycled to the extraction column. The extracted solutes are depressurized to remove residual CO_2 and this concentrate is then detoxified (by, e.g., incineration).

The cost breakdown for treating aqueous wastes by CO_2 extraction has not been made public. However, CFS has published costs for extracting acetic acid from an aqueous phase [14] and those costs have been used herein as a guide to estimate costs for a hazardous waste application.

The costs are given in Table 5. The acetic acid extraction was evaluated as a separation step in acetic acid manufacture; the 20 wt% feed and 1 wt% effluent concentrations are out of the range of consideration in waste applications. On the other hand, a 45-tray extractor is not unreasonable for aqueous waste treatment.

With the exception of supervision and labor overhead, the costs for the acetic acid case were published by CFS [14]. The total annual cost of $1.9 million and unit cost of $0.04/gal were computed for an aqueous feed rate of 200,000 ton/yr which is equivalent to about 100 gal/min.

The acetic acid costs were extrapolated to the extraction of an aqueous waste from acrylonitrile manufacture. The conditions of extraction and separation as well as the variable costs were published by CFS following laboratory investigation [15]. Note that an 86-tray column is required for 99.9% removal of organics (2900 ppm influent to 4 ppm effluent). The semivariable and fixed costs were estimated by the author. The total annual cost of $900,000 and the unit cost of $0.09/gal are quite attractive, even for the relatively small feed rate of 20 gpm. (A typical world-class acrylonitrile plant will generate from 100 to 400 gpm.) Note that the fixed cost is 60% of the total; thus, the unit cost should decrease appreciably with increasing throughput.

The applicability of CO_2 extraction depends upon the type of organic present in the waste. The pertinent design parameter is the distribution coefficient of organic between CO_2 and water phases. Table 6 is a compilation from data published by CFS for organics in CO_2 with and without cosolvent [16]. Note that the distribution coefficient increases with increasing hydrophobicity. For the acetic acid separation described in Table 5 (25 wt% capyrlic acid cosolvent), the distribution coefficient was probably close to 0.5; for the acrylonitrile/acetonitrile case, the limiting solute was acetonitrile, which has the lower distribution coefficient of 0.75. Even for these relatively hydrophilic organics, CO_2 extraction is economically viable.

FIGURE 4. EXTRACTION OF SOLUTES FROM AQUEOUS STREAMS WITH SCF CO_2
(SOURCE: Critical Fluid Systems, Inc.)

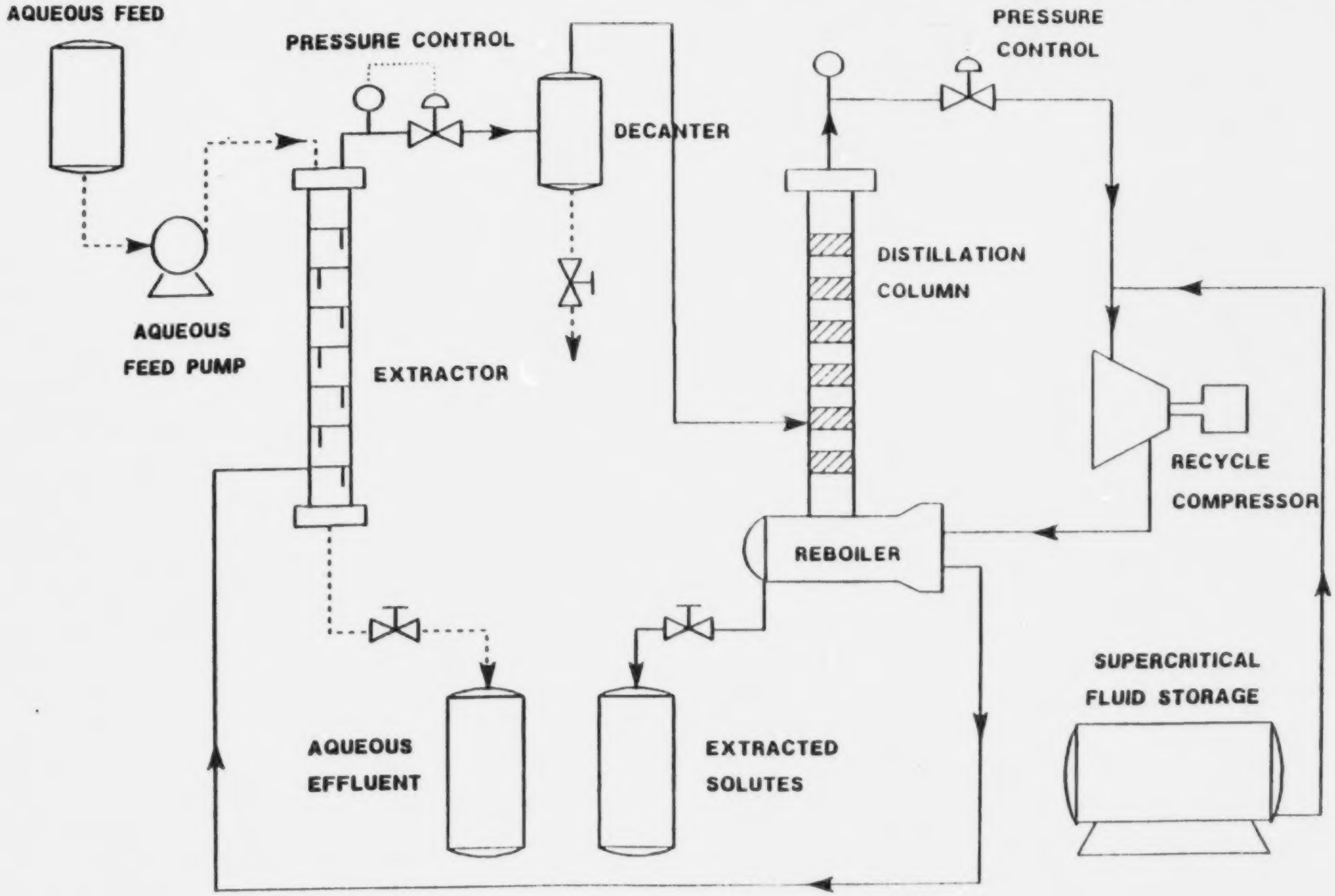

AQUEOUS FEED
PRESSURE CONTROL
DECANTER
PRESSURE CONTROL
DISTILLATION COLUMN
AQUEOUS FEED PUMP
EXTRACTOR
RECYCLE COMPRESSOR
REBOILER
SUPERCRITICAL FLUID STORAGE
AQUEOUS EFFLUENT
EXTRACTED SOLUTES

TABLE 5

COST ESTIMATES FOR CARBON DIOXIDE EXTRACTION OF ORGANICS FROM AQUEOUS WASTES

WASTE COMPONENTS	Acetic acid	Acrylonitrile Acetonitrile
REFERENCE	[14]	[15]
BASIS		
Operating hours	8,000 hr/yr	8,000 hr/yr
Feed rate	200,000 ton/yr 100 gpm	40,000 ton/yr 20 gpm
Feed concentration	20 wt%	2,900 ppm
Effluent concentration . . .	1 wt%	4 ppm
Solvent:feed ratio	2.0	1.5
Solvent flow rate	100,000 lb/hr	15,000 lb/hr
Cosolvent	Caprylic acid	none
Cosolvent loading	25 wt%	
Extractor temperature		27°C
Extractor pressure		75 atm
No. of extractor trays . . .	45	86
Distillation temperature . .		16°C
Distillation pressure		51 atm
ESTIMATED ANNUAL COSTS ($000)		
Variable Costs		
Electricity	200	60
Steam	270	10
Water	20	20
Solvent make-up	40	10
	530	100
Semivariable Costs		
Labor	120	100
Supervision	20 *	20 *
Overhead	140 *	120 *
	280	240 *
Fixed Costs		
Depreciation	680	340 *
Maintenance	270	140 *
Taxes & insurance	100	50 *
	1,050	530 *
Total Annual Cost ($000)	1,860	870 *
Unit Cost ($/gal waste)	0.039	0.092 *

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* Estimates by author

TABLE 6

DISTRIBUTION COEFFICIENTS AND EFFICIENCIES OF CARBON DIOXIDE EXTRACTION OF ORGANICS FROM WATER [15,16]

SOLUTE	COSOLVENT	COSOLVENT LOADING (wt%)	DISTRIBUTION COEFFICIENT	EFFLUENT FROM A 25 TRAY EXTRACTOR (calculated)	
				CONC. (ppm)	REMOVAL (%)
Acetic acid	caprylic acid	0	0.066		
Acetic acid	caprylic acid	5	0.104		
Acetic acid	caprylic acid	10	0.35		
Acetic acid	caprylic acid	20	0.43		
Methanol			0.10	8600.	14
Isopropyl alcohol			0.26	6200.	38
Acetonitrile			0.75	500.	95
Acetone			1.10	30.	99.7
Acrylonitrile			5.	0.16	>99.9
Methyl isobutyl ketone			14.	0.06	>99.9
Trichloroethylene			17.	0.05	>99.9
Carbon Tetrachloride			21.	0.04	>99.9
Methyl Methacrylate			25.	0.04	>99.9
Xylene			45.	0.02	>99.9

The last column of Table 6 is the calculated removal efficiency for a 25-tray extraction column. The effluent concentration given in Table 6 corresponds to an influent of 1 wt%. It can be seen from these results, taken together with the estimated costs given in Table 5, that CO_2 extraction of aqueous wastes may have broad applicability.

SUPERCRITICAL WATER OXIDATION

1. Properties of Supercritical Water

Above the critical temperature and pressure, the properties of water are quite different from that of the normal liquid or atmospheric steam. The critical point (C.P.), which lies on the vapor-liquid saturation dome, occurs at 374°C, 22.1 MPa and 0.3 g/cm^3.

Properties as a function of temperature at a supercritical pressure of 25 MPa are shown in Fig. 5. The density decreases slowly from room temperature to 200°C and somewhat faster up to the supercritical fluid region. Above 380°C, the density decreases very rapidly with temperature. Beyond 410°C, the rate of change decreases again. The solubilities of benzene and heptane in water are shown in Fig. 5 [17,18]. At 25°C, benzene is sparingly soluble in water (0.07 wt%). Between 260°C and 300°C, benzene solubility increases from a few percent to completely miscible. Aliphatics exhibit similar solubility behavior, but at slightly higher temperatures. In general, organics and water are miscible in all properties above the critical temperature of water.

The solubility of sodium chloride in water, as illustrated in Fig. 5, is representative of the behavior of strong electrolytes. At 25 MPa, the solubility increases gradually from room temperature to a maximum at 450°C, at which temperature a phase transition occurs: the dense fluid phase disappears in favor of solid NaCl [19]. The residual solubility of NaCl in the supercritical water phase is the order of 100 ppm. Given the fact that the dielectric constant of water is about 2 at 450°C and 25 MPa, it is not surprising that inorganics are practically insoluble.

Coincident with the loss of solvating power for inorganic salts, supercritical water also loses the ability to dissociate salts. For example, the dissociation constant of NaCl at 400 to 500°C and densities in the range of 0.35 is of the order of 10^{-4} [20]. Thus, strong electrolytes become weak electrolytes in supercritical water.

Destruction efficiencies (DE) for SCWO have been reported for many organics, a compilation of which is given in Table 7. These data were fitted with first order kinetics to generate the oxidation conversion curves shown in Fig. 5.

In general, DE's of the order of 99 to 99.9% can be obtained at 400 to 500°C with 1 to 5 min residence time; 99.99% at 500 to 550°C with about 1 min; and 99.999% at 550 to 600°C with less than 1 min. It has also been stated that 99.9999% is achievable at 600 to 650°C with a residence time of seconds [24], but such data have not been published.

2. The Modar Process

This process has been under development since 1980. As practiced by Modar, it is intended for use with moderately concentrated aqueous wastes. A schematic for a process for treating an aqueous waste containing 10 wt% organic is given in Fig. 6 [23]. This process consists of the following steps:

FIGURE 5.
PROPERTIES OF WATER AT 25 MPa

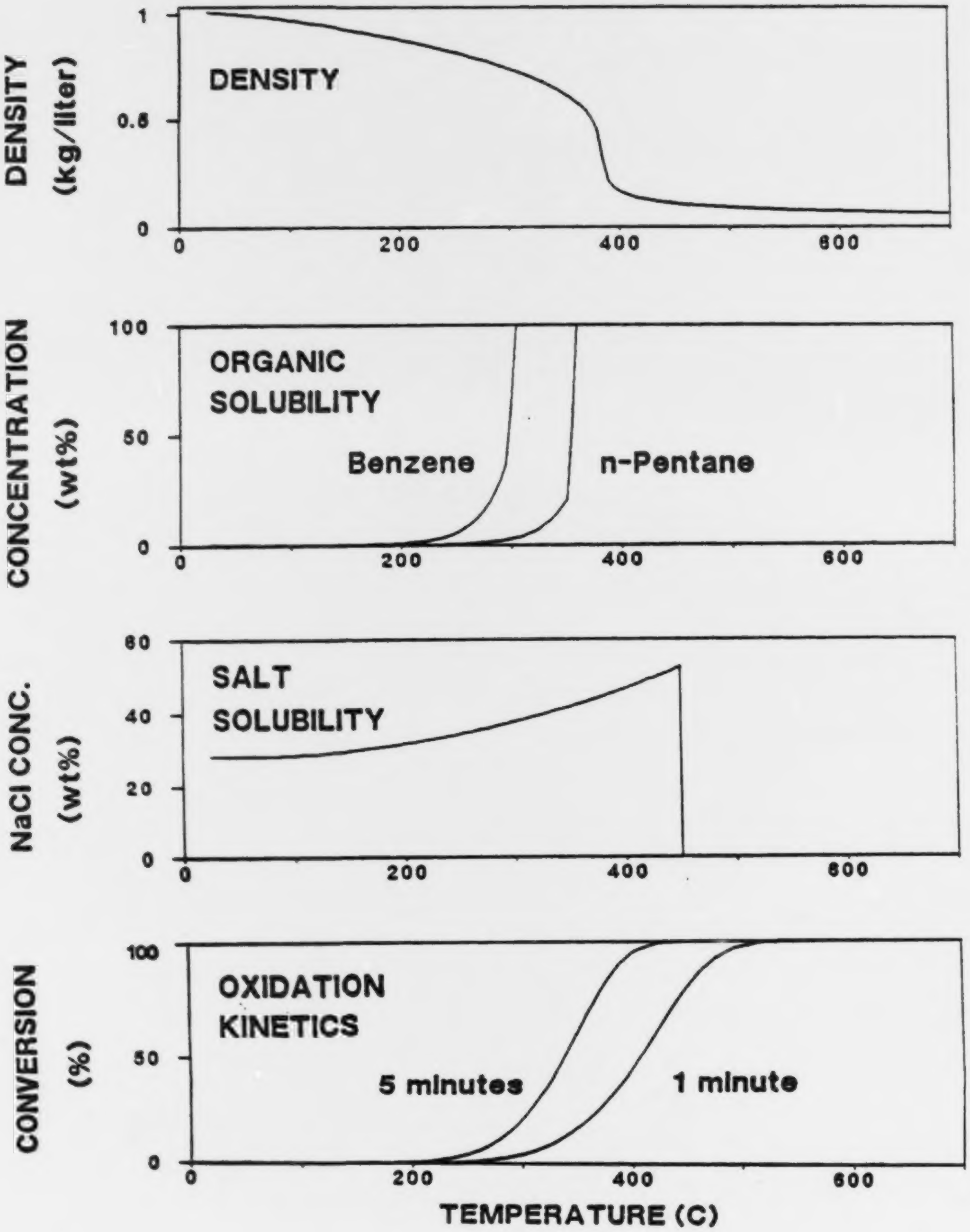
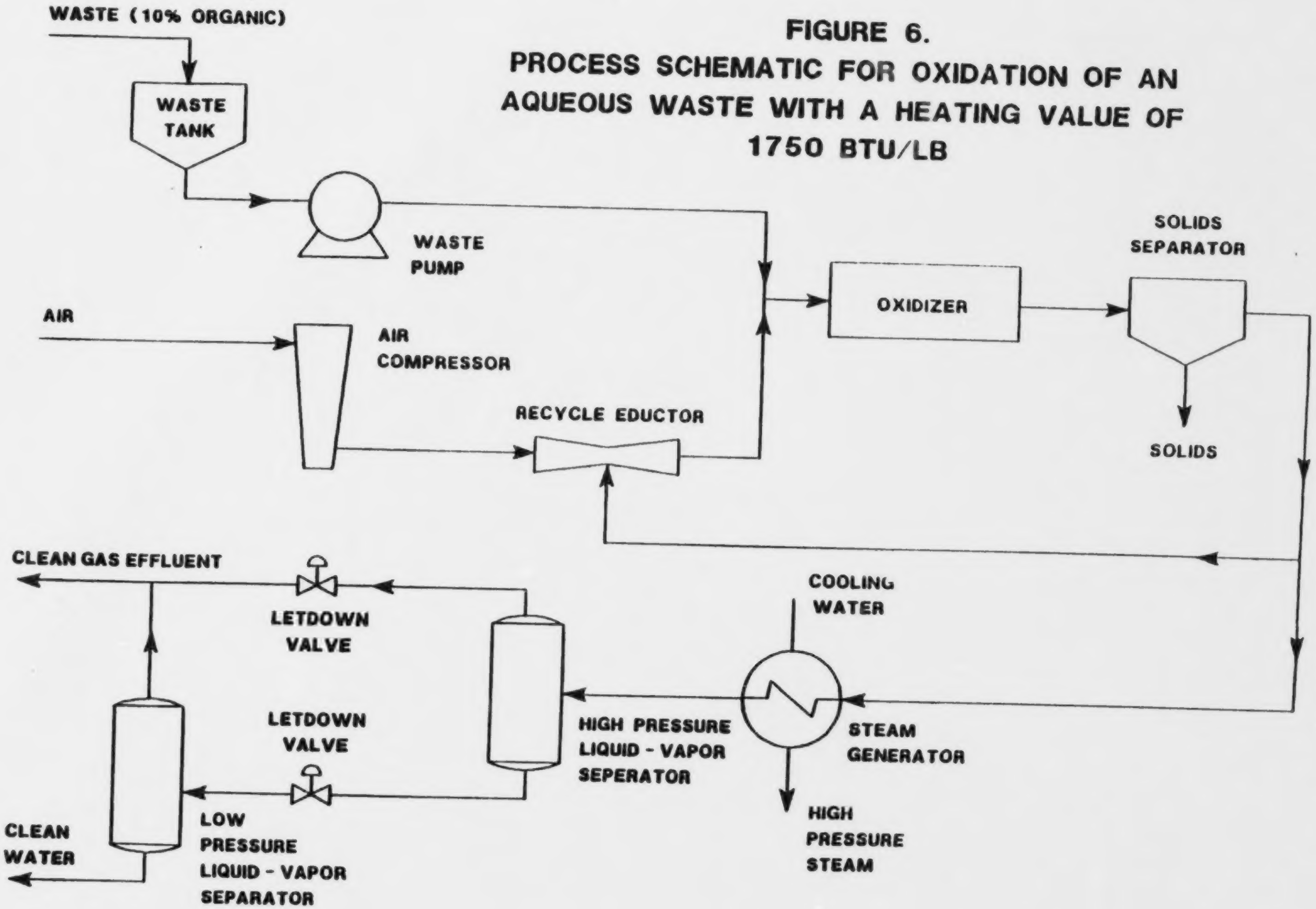


TABLE 7

DESTRUCTION EFFICIENCIES OF ORGANICS BY SUPERCRITICAL WATER OXIDATION

CLASS/ COMPOUND	TEMPER-ATURE (C)	RESIDENCE TIME (min)	DESTRUCTION EFFICIENCY (%)	REF.
Aliphatic Hydrocarbons				
Cyclohexane	445	7.	99.97	[21]
Aromatic Hydrocarbons				
Biphenyl	450	7.	99.97	[21]
o-Xylene	495	3.6	99.93	[22]
Halogenated Aliphatics				
1,1,1-Trichloroethane	495	3.6	99.99	[22]
1,2-Ethylene dichloride	495	3.6	99.99	[22]
1,1,2,2-tetrachloroethylene	495	3.6	99.99	[22]
Halogenated Aromatics				
o-chlorotoluene	495	3.6	99.99	[22]
Hexachlorocyclopentadiene	488	3.5	99.99	[22]
1,2,4-Trichlorobenzene	495	3.6	99.99	[22]
4,4-Dichlorobiphenyl	500	4.4	99.993	[22]
DDT	505	3.7	99.997	[22]
PCB 1234	510	3.7	99.99	[22]
PCB 1254	510	3.7	99.99	[22]
Oxygenated Compounds				
Methyl ethyl ketone	460	3.2	99.96	[21]
Methyl ethyl ketone	505	3.7	99.993	[22]
Dextrose	440	7.	99.6	[21]
Organic Nitrogen Compounds				
2,4-Dinitrotoluene	457	0.5	99.7	[23]
2,4-Dinitrotoluene	513	0.5	99.992	[23]
2,4-Dinitrotoluene	574	0.5	99.9998	[23]

FIGURE 6.
PROCESS SCHEMATIC FOR OXIDATION OF AN AQUEOUS WASTE WITH A HEATING VALUE OF 1750 BTU/LB


WASTE (10% ORGANIC)
WASTE TANK
WASTE PUMP
AIR
AIR COMPRESSOR
RECYCLE EDUCTOR
OXIDIZER
SOLIDS SEPARATOR
SOLIDS
COOLING WATER
STEAM GENERATOR
HIGH PRESSURE STEAM
HIGH PRESSURE LIQUID - VAPOR SEPERATOR
LETDOWN VALVE
LETDOWN VALVE
CLEAN GAS EFFLUENT
LOW PRESSURE LIQUID - VAPOR SEPARATOR
CLEAN WATER

1. The waste, as either an aqueous solution or a slurry, is pressurized and delivered to the oxidizer inlet. It is heated to supercritical conditions by direct mixing with recycled reactor effluent.
2. Oxygen is supplied in the form of compressed air, which is used as the motive fluid in an eductor to provide recycle of a portion of the reactor effluent. This inlet mixture is then a homogeneous phase of air, organics and supercritical water.
3. The organics are oxidized in a controlled but rapid reaction. The heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly.
4. The effluent from the oxidizer is fed to a cyclone. Inorganic salts that are originally present in the feed or which form in the combustion reactions precipitate out of the fluid phase in the oxidizer and are separated here.
5. The fluid effluent of the solid separator is a mixture of H_2O, N_2, and CO_2. A portion of this is recycled through the eductor to provide supercritical conditions at the oxidizer inlet.
6. The remainder of the effluent is available as a high temperature, high pressure fluid for energy recovery. This stream is cooled to a subcritical temperature in a heat exchanger which serves to generate low pressure or high pressure steam.
7. Now at a subcritical temperature, the mixture has formed two phases and enters a high pressure liquid-vapor separator. Practically all of the N_2 and most of the CO_2 leaves with the gas stream. The liquid consists of water with an appreciable amount of dissolved CO_2.
8. The gas stream can then be expanded through a turbine to extract the available energy as power. A portion of the power is used for compression of the inlet air.
9. The liquid from the high pressure separator is depressurized and fed to a low pressure separator. The vapor stream is primarily CO_2 which is vented with the gas turbine effluent. The liquid stream is clean water.

Since no commercial installations have yet been built, the published costs should be considered only as estimates.

Table 8a contains cost estimates recently published by Modar for a unit with a capacity of 10 ton/day of a waste with 10 wt% organic. Since these estimates provide both capital and operating costs, one can extrapolate from these to other throughputs. Table 8b was generated from the estimates of Table 8a on the assumption that the capital cost follows a 0.6 power with throughput. Two sets of costs are shown in Table 8b for capital recovery factors of 25 and 12%, respectively.

These estimated costs compare very favorably to incineration of aqueous wastes with comparable heating value [25]. For throughputs higher than 10 to 20 TPD organic, the total estimated costs of SCWO treatment are less than the fuel costs alone of liquid injection incineration with effluent scrubbers.

3. The Oxidyne Process

Oxidyne has proposed to conduct wet oxidation and supercritical water oxidation in reactors which are placed underground in deepwell-like cavities. The processes have been referred to as "downhole" oxidation. This variation of SCWO is particularly well-suited to large flow rates of dilute aqueous wastes.

TABLE 8a

COST ESTIMATES FOR SUPERCRITICAL WATER OXIDATION OF ORGANICS

PROJECTED COSTS FOR 10 TON/DAY THROUGHPUT [21]

Annual capacity . . . . 3,300 ton/year

Capital Costs

Tanks, Pumps, Eductor
Heat Exchanger, Reactor and Instrumentation
Separators, Let-Down Units, Start-up Furnace
Air Compressor
Contingencies

Capital Cost Estimate $5,320,000

Processing Costs

Chemicals and Utilities (Elec @ $.04/kW-hr; Water @ $.055/million gal)
Operating Labor and Plant Overhead
Maintenance (5% of capital cost estimate)
By-Product Steam Credit ($6/million lb)
Cost Capital (25% of capital cost estimate)

Total Operating Cost $2,143,000

Unit Cost ($/gal organic) $2.38

Unit Cost($/gal wastewater; 10% organic content) $0.26

TABLE 8b

EXTRAPOLATED COSTS FOR AN AQUEOUS WASTE WITH 10 wt% ORGANIC*

Throughput		Capital Cost Estimate ($ M)	Operating Costs ($/gal)	
Organic (TPD)	Waste (GPM)		25% Capital Recovery	12% Capital Recovery
2	3	2.0	0.43	0.27
4	7	3.1	0.35	0.22
8	14	4.7	0.28	0.19
10	17	5.3	0.26	0.18
12	21	5.9	0.25	0.17
20	35	8.1	0.21	0.15
50	87	14.	0.17	0.12
100	174	21.	0.14	0.11

---

* Estimates by author

A schematic is shown in Fig. 7. Oxygen is compressed and fed to a central downcomer. Waste is pressurized and fed to an inner annulus. The waste is heated by countercurrent exchange with reaction effluent in the outer annulus. At some depth, which may be 1,000 to 3,000 m, the waste reaches supercritical conditions. Oxygen and waste are then combined and supercritical oxidation ensues. The reacting mixture reverses flow at the bottom of the reactor and cools during upflow in the outer annulus.

The effluent from the downhole reactor undergoes depressurization and vapor phase separation (see Fig. 7). The liquid effluent is cooled to ambient and recirculated in a solids growth tank to provide residence time for inorganic oxides and ash to agglomerate. The final step is liquid-solid separation.

The Oxidyne process differs from that of Modar in several respects. Oxidyne conducts the oxidation at lower temperatures (<450°C) where inorganic salts do not precipitate out in the reactor. As a consequence of the lower temperature, a longer residence time is required. The downhole process might be expected to require 1 to 5 min at 400 to 450°C to reach 99 to 99.9% destruction efficiency.

The downhole reactor is, in reality, a combined heat exchanger and reactor. The heat exchanger area provided by 1,000 to 3,000 m of pipe, combined with the excellent insulation provided by the earth, results in extremely efficient energy utilization. Thus, Oxidyne projects that the downhole process can be applied to aqueous wastes with as little as 1 wt% organic [26].

Processing cost projections for the downhole process are shown in Fig. 8 [27]. Note that the throughputs for the downhole process are considerably higher than those for the surface process, given in Table 8. For 100 gpm, where the two costs projections overlap, both are in the range of $.10 to .15 per gallon. At throughputs above 200 gpm, Oxidyne projects costs below $.10/gal, and possibly as low as $.07/gal. Such costs are not much higher than the present cost of deepwell injection. Thus, downhole SCWO presents the promise of an oxidative destruction at costs that are comparable to that of current disposal practice.

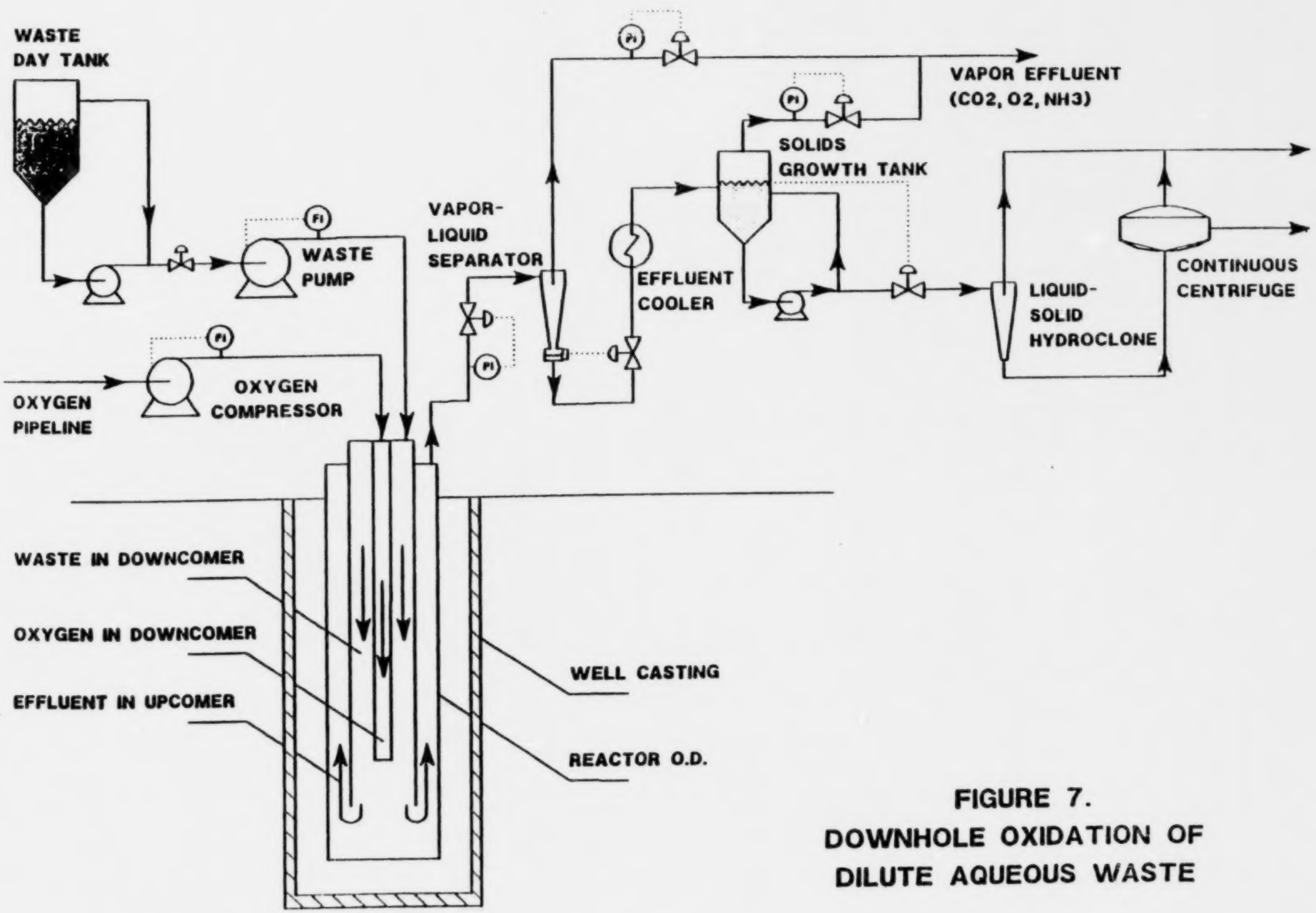
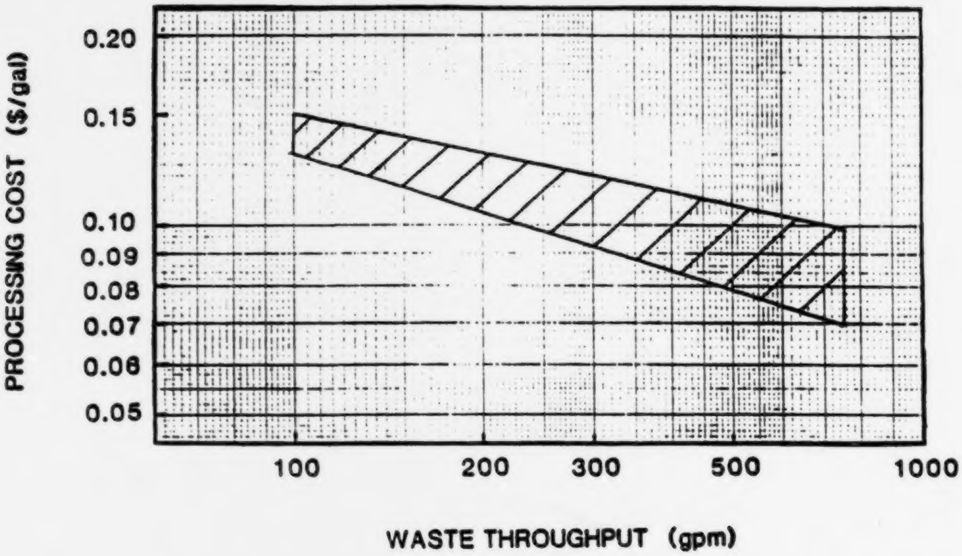

WASTE DAY TANK
WASTE PUMP
FI
OXYGEN PIPELINE
OXYGEN COMPRESSOR
VAPOR-LIQUID SEPARATOR
PI
EFFLUENT COOLER
SOLIDS GROWTH TANK
VAPOR EFFLUENT (CO2, O2, NH3)
LIQUID-SOLID HYDROCLONE
CONTINUOUS CENTRIFUGE
WASTE IN DOWNCOMER
OXYGEN IN DOWNCOMER
EFFLUENT IN UPCOMER
WELL CASTING
REACTOR O.D.

FIGURE 7.
DOWNHOLE OXIDATION OF
DILUTE AQUEOUS WASTE

FIGURE 8.

PROCESSING COSTS FOR SUPERCRITICAL WATER OXIDATION OF AQUEOUS WASTES (Source: Oxidyne, Inc.)



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Oxidyne.

Dr. George Hartmann

A COMPANY SPECIALIZING IN THE DESIGN, CONSTRUCTION, AND OPERATION OF WASTE DISPOSAL FACILITIES EMPLOYING DEEP WELL REACTOR TECHNOLOGY

THE OXIDYNE COMPANY

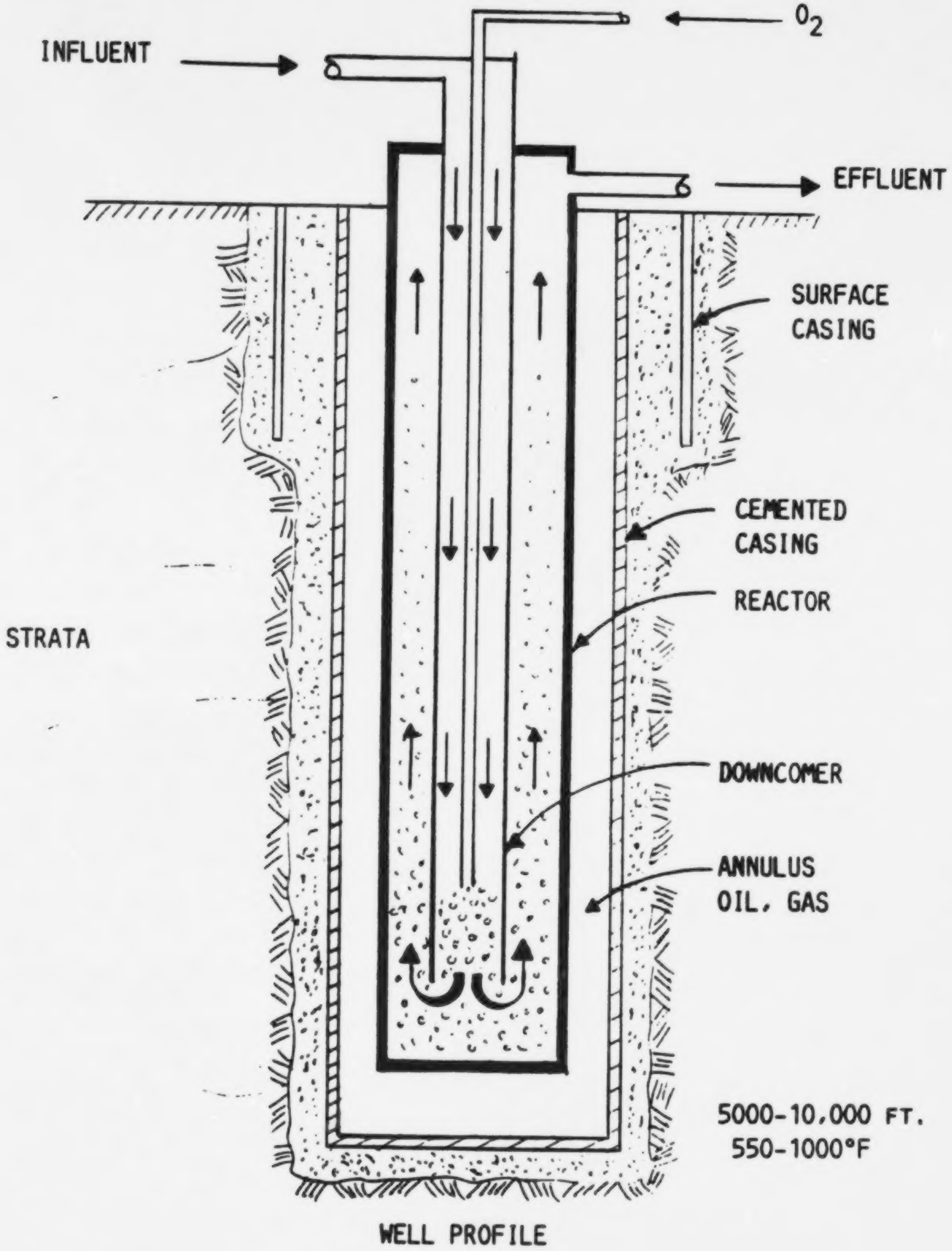
- U.S. COMPANY FORMED IN 1984
- PROVIDES PROJECT FINANCING, DESIGN CONSTRUCTION AND OPERATION OF TECHNOLOGY
- HOLDS 5 U.S. DEEP WELL PATENTS
- IS PURSUING PROJECTS WORLDWIDE

WET AIR OXIDATION HISTORY

1830s	PHENOMENA OF "WET" COMBUSTION FIRST OBSERVED IN LABORATORY
1880s	FIRST RECORDED DEFINITIVE LABORATORY TESTS YIELDING DATA ON WAO PHENOMENA
1910s	CHEMICAL INDUSTRY LOOKS AT WAO PROCESS FOR CHEMICAL INDUSTRY
1940s & 50s	ZIMMERMAN OBTAINS PATENT ON ZIMPRO PROCESS FOR TREATMENT OF ORGANIC WASTES
1957	ZIMPRO BUILDS FIRST HIGH PRESSURE WAO SYSTEM IN U.S.

PATENTS CURRENTLY HELD BY OXIDYNE

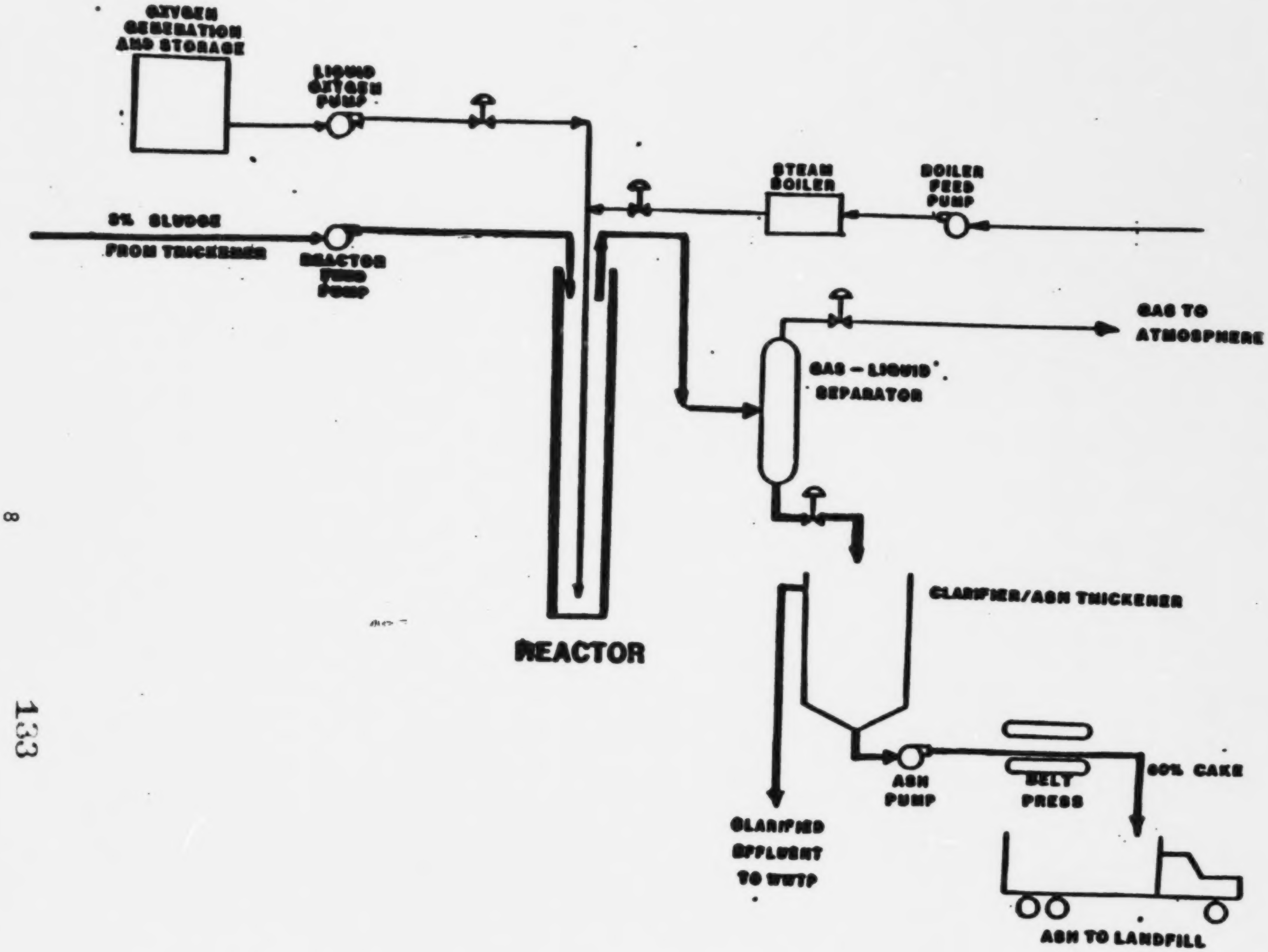
INVENTOR (YEAR ISSUED)	U.S. PATENT NUMBER	DESCRIPTION
SUBCRITICAL PATENTS		
BAUER (1969)	3,449,247	PROCESS FOR WET OXIDATION OF COMBUSTIBLE WASTE MATERIALS (SUBCRITICAL)
LAWLESS (1971)	3,606,999	METHOD FOR CARRYING OUT A CHEMICAL OR PHYSICAL PROCESS (DEEP WELL SUBCRITICAL)
TITMAS (1974)	3,853,759	DYNAMIC COLUMN ACTIVATION METHOD (DEEP WELL PYROLYSIS)
SUPERCRITICAL WATER PATENTS		
BURLESON (1986)	4,564,458	METHOD AND APPARATUS FOR DISPOSAL OF A BROAD SPECTRUM OF WASTE FEATURING OXIDATION OF WASTE (SUPERCRITICAL OXIDATION)
TITMAS (1986)	4,594,164	METHOD AND APPARATUS FOR CONDUCTING CHEMICAL REACTIONS AT SUPERCRITICAL CONDITIONS (DEEP WELL OXIDATION)


O_2
INFLUENT
EFFLUENT
SURFACE CASING
CEMENTED CASING
REACTOR
STRATA
DOWNCOMER
ANNULUS OIL, GAS
5000-10,000 FT.
550-1000°F

WELL PROFILE

TYPICAL OXIDATIVE PERFORMANCE

- 97-99% VOLATILE SOLIDS DESTRUCTION
- 80-85% COD REDUCTION
- STERILE NON-TOXIC ASH
- RECOVERY OF 30 TO 70% OF INFLUENT ORGANIC BTU'S
- ODOR FREE OPERATION
- SMALL LAND AREA REQUIRED


OXYGEN GENERATION AND STORAGE
LIQUID OXYGEN PUMP
8% SLUDGE
FROM THICKENER
REACTOR FEED PUMP
STEAM BOILER
BOILER FEED PUMP
GAS TO ATMOSPHERE
GAS – LIQUID SEPARATOR
CLARIFIER/ASH THICKENER
REACTOR
ASH PUMP
BELT PRESS
60% CAKE
CLARIFIED EFFLUENT TO WWTP
ASH TO LANDFILL

OXIDYNE - VERTECH PROCESS DIFFERENCES

- OXIDYNE DOES NOT USE SEPARATE CLOSED LOOP HEAT EXCHANGER IN REACTOR
    - PROVIDES BETTER UTILIZATION OF REACTOR CROSS SECTION
- OXIDYNE USES FINE BUBBLES RATHER THAN VERTECH TAYLOR BUBBLE
    - FINE BUBBLES PROVIDE BETTER OXYGEN MASS TRANSFER
- OXIDYNE INTRODUCES OXYGEN DEEP IN REACTOR
    - HYDROLYSIS TAKES PLACE SEPARATELY FROM OXIDATION
    - INJECTED OXYGEN TAKES UP SMALL VOLUME IN REACTOR
    - BETTER OXYGEN SOLUBILITY AT HIGH INJECTION PRESSURE AND TEMPERATURES

OXIDYNE HOUSTON CONTRACT CHRONOLOGY

- CITY UNDER STATE AND EPA ORDERS TO BRING SEWAGE AND SLUDGE DISPOSAL SYSTEMS INTO COMPLIANCE
- GCA HAS MANDATE TO PROVIDE LEADERSHIP IN STATE FOR WASTE TREATMENT AND DISPOSAL
- GCA HAD SLUDGE TREATMENT AND DISPOSAL STUDIES UNDERWAY FOR ITS OWN WASTE WATER TREATMENT FACILITIES
- GCA ASKED BY CITY TO HELP CITY SOLVE SLUDGE DISPOSAL PROBLEM
- GCA AND CITY EVALUATE ALTERNATIVE SLUDGE TREATMENT AND DISPOSAL TECHNOLOGIES
- GCA SELECTS BEST PROCESSES

GCA HOUSTON SLUDGE DISPOSAL EVALUATION

- INDEPENDENTLY GCA EVALUATED BEST PROCESSES
    - OXIDYNE
    - CARVER GREENFIELD
    - VERTECH
    - LAND DISPOSAL
    - INCINERATION

- GCA & HOUSTON DETERMINED SLUDGE DESTRUCTION PROCESS BEST LONG-TERM SOLUTION

- GCA/CITY EVALUATION TOOK 1 YEAR

OXIDYNE DEEP WELL PROCESS SELECTED FOR THE FOLLOWING REASONS:

- ODOR FREE OPERATION
- NON HAZARDOUS ASH
- SMALL LAND REQUIREMENT
- EASILY PERMITTED—NOT INCINERATION—NO STACK GASES
- SHORT DESIGN AND CONSTRUCTION TIME
- COST COMPETITIVE
- USES OFF THE SHELF EQUIPMENT AND TECHNOLOGY
- GCA & CITY COMFORTABLE WITH WELL DRILLING AND COMPLETION TECHNOLOGY USED BY OXIDYNE

REASON FOR OXIDYNE SELECTION

- PRICE COMPETITIVE—$215-230/DT FOR 35-55 DT/D OF SLUDGE
- ADDITIONAL 20% PRICE DISCOUNT OFFERED WHEN OXIDYNE CONVERTS UNIT TO SCW PROCESS

OXIDYNE HOUSTON PROJECT STATUS

- APPLYING FOR PERMITS NOW (60-90 DAYS FOR ISSUANCE)
- WILL MOVE ONTO SITE IN 30 DAYS
- CONSTRUCTION TO BEGIN IN SUMMER
- PLANT START-UP SCHEDULED FOR LATE SEPTEMBER, 1989
- 1 YEAR PROTOTYPE OPERATION
- 18-YEAR LENGTH CONTRACT

CONTRACT INFORMATION
MAJOR REQUIREMENTS

1) 18-YEAR CONTRACT BETWEEN OXIDYNE AND GCA AND GCA AND CITY OF HOUSTON

2) OXIDYNE PROCESS A MINIMUM OF 40 TONS/DAY OF SLUDGE FOR FIXED PRICE/TON

3) CITY PAYS FOR A MINIMUM OF 35 TONS/DAY OF SLUDGE

4) RECYCLE STREAM TO CITY MEETS THE FOLLOWING:

    A. LESS THAN 150 LBS. COD/DRY TON OF SLUDGE PROCESSED
    B. LESS THAN 125 LBS. TSS/DRY TON OF SLUDGE PROCESSED
    C. MEET CITY INDUSTRIAL PRETREATMENT STANDARDS

5) MEET ALL AIR QUALITY EMISSION REQUIREMENTS

6) PROVIDE ALTERNATIVE SLUDGE PROCESSING AND DISPOSAL SYSTEM

7) ACHIEVE 90% PLUS ON-LINE TIME

8) OXIDYNE PROVIDES ALL FUNDS FOR DESIGN, CONSTRUCTION AND OPERATION

9) DURING 1ST YEAR OF OPERATION, OXIDYNE MUST DEMONSTRATE PLANT MEETS CONTRACT OPERATING REQUIREMENTS

10) JOINT OPERATING PERMIT BETWEEN GCA AND OXIDYNE

Oxidyne Sims Bayou Processing Facility

Capacity	40-70 Dry Tons/Day
Sludge Concentration & Flow	2-3% TSS @ 200-400 gpm
Max. Temperature	650°F
Max. Pressure	2600 psig
Land Requirements	2-1/4 Acres
COD Reduction	75 -90%
VSS Reduction	More than 98%
Oxygen Required	35-45 Tons/Day of liquid oxygen
Residual Dewatered Ash (40-50% moisture content)	12-15 Dry Tons/Day 25-30 Wet Tons/Day (30 CY/Day)
Ash Characteristics	Non-Hazardous: passes EPA TCLP TEST
Ash Disposition	Sanitary Landfill
Operating Hours	24 Hr./Day 7 Days/Week

REACTOR AND WELL INFORMATION

REACTOR -	10-12" DIAMETER, 5,000 FT. LONG
WELL CASING -	16" - 20" DIAMETER 2,200 FT. SURFACE CASING 13-3/8" - 16" 5,000 FT. WELL CASING ALL CARBON STEEL
CEMENTING -	FULL LENGTH OF WELL CASING AND SURFACE CASING CEMENTED TO SURFACE

MAJOR OPERATING PROCESS EQUIPMENT

A) SLUDGE HOLDING AND THICKENING

B) INFLUENT PUMPING AND FLOW CONTROL

C) OFFGAS SEPARATION AND EXCESS HEAT REMOVAL

D) SOLIDS SEPARATION

E) EFFLUENT POLISHING

F) SOLIDS DEWATERING

G) OXYGEN FEED

STARTUP & MAINTENANCE SYSTEMS

A) STEAM BOILER SYSTEM (REACTOR HEATUP) -

B) SCALE REMOVAL - (NITRIC ACID WASH) - ONCE - TWICE/MONTH

C) LIME FEED FOR ALTERNATIVE SLUDGE TREATMENT

PERSONNEL REQUIREMENTS

OPERATORS: 6-9

MAINTENANCE: 2-3

REACTOR AND WELL INFORMATION

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WET AIR OXIDATION OF OILS, OIL REFINERY SLUDGES, AND SPENT DRILLING MUDS

By

William M. Copa

and

Marvin J. Dietrich

ZIMPRO/PASSAVANT INC.

April, 1988

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ABSTRACT

Wet air oxidation is a process that accomplishes an aqueous phase oxidation of organic or inorganic substances. The oxidation reaction is conducted at elevated temperatures of 175 to 320°C and pressures of 300 to 3000 psig.

In the present study, wet air oxidation was applied to heavy oils, wellhead oils, RCRA hazardous oily sludges that are generated in the treatment of produced water, and spent drilling muds. The application of wet air oxidation to these materials is discussed. The results of the present study show that wet air oxidation can be used to oxidize oils and recover energy, dispose of oily wastes and waste oils, and to effect the dewatering of spent drilling muds.

Introduction

The disposal of waste oils and refinery sludges is a topic that is currently receiving much attention. The Environmental Protection Agency is in the process of developing treatment standards for a variety of Resource Conservation and Recovery Act (RCRA) listed hazardous wastes. Some of these treatment standards will be directed toward the petroleum refining industry. The specific wastes from the refining industry that will be subjected to these treatment standards are the dissolved air flotation (DAF) float (K048), slop oil emulsion solids (K049), API separator sludge (K051), and tank bottoms (K052).

In the past few years, there has also been a move to classify all waste oils as RCRA hazardous waste and to regulate the disposal of these materials. At present waste oils are only classified as RCRA hazardous waste if they exhibit the hazardous characteristics (pH, flammability, corrosivity, or EP Toxicity).

Waste oils and sludges from the oil refining industry contain organic hydrocarbons. The wet air oxidation process can effectively oxidize organic hydrocarbons. It would appear then that the wet air oxidation process would be ideally suited for disposal of waste oils and sludges from the oil refining industry.

The wet air oxidation process, developed over the past fifty years (1-4), has been extensively applied to treatment of municipal sewage treatment plant sludge and industrial wastewater. Approximately 200 wet air oxidation units have been installed and operated for a variety of waste disposal or wastewater treatment objectives(5).

The purpose of this paper is to discuss the application of wet air oxidation to the disposal of waste oils and oily wastes. Bench scale wet air oxidation work, on various oils and oily wastes, is reported and interpreted.

The Wet Air Oxidation Process

Wet air oxidation is a process that accomplishes an aqueous phase oxidation of organic or inorganic substances at elevated temperatures and pressures. The usual temperature range varies from approximately 350 to 600°F (175 to 320°C). System pressures of approximately 300 to 3000 psig are used to limit the amount of evaporation of water at the desired reaction temperature. Compressed air or pure oxygen is the source of oxygen that serves as the oxidizing agent in the wet air oxidation process.

The basic flow diagram for the wet air oxidation process is shown in Figure 1. In processing an aqueous waste, the waste stream containing the oxidizable material is first pumped into the system using a positive displacement, high pressure pump. Next, the waste is preheated in a heat exchanger with the hot oxidized effluent. The compressed air or oxygen is injected into the waste stream either at the discharge of the high pressure pump or at the inlet to the reactor. A vertical bubble column is commonly used as the reactor which provides the required hydraulic detention time to effect the desired reaction. The desired reaction may range from a mild oxidation, which requires a few minutes, to total waste destruction, which requires an hour or more detention time. Exothermic heat of oxidation is released to the waste stream during oxidation. This heat release usually raises the temperature of the waste stream to the desired level in the reactor. The hot, oxidized effluent exits the reactor and is cooled in the process heat exchangers. The cooled effluent then exits the system through a pressure control valve. The oxidized liquid and non-condensible offgases are separated in a separator tank and discharged through separate lines.

The products of wet air oxidations vary with the degree of oxidation that is accomplished. For low degrees of oxidation, oxidizable organic matter is converted to low molecular weight organic compounds such as acetic acid. For high degrees of oxidation, oxidizable organic matter is chiefly converted to carbon dioxide and water. Organic or inorganic sulfur is converted to sulfate. Organic nitrogen is converted primarily to ammonia. The halogens in halogenated organics are converted to inorganic halides.

The commercial applications of wet air oxidation are chiefly in the disposal of aqueous wastes. However, some applications employ wet air oxidation for recovery of chemicals and energy production, simultaneously with waste disposal.

Bench Scale Testing of Wet Air Oxidation

Wet air oxidation has been applied to the disposal of oils and oily sludges from the refinery industry in a variety of bench scale studies. These studies have been conducted at the Zimpro/Passavant laboratory facility in Rothschild, Wisconsin. Bench scale wet air oxidation studies have been conducted on produced waters, wellhead oils, heavy oils, oily sludges from the refinery industry, and spent drilling muds.

The bench scale studies were conducted using batch autoclaves which were constructed from titanium. The batch autoclaves were either the shaking type, with a total volume of 500 ml, or the stirred type, with a total volume of 1.0 gallon. In conducting the autoclave tests, the autoclave was charged with the waste sample, sealed, and charged with a sufficient quantity of air or oxygen to satisfy the autoclave oxygen demand (AOD). The autoclave was then heated to temperature while continuously being agitated by either the rocking action of the shaking autoclave assembly or by the magnetically coupled stirring assembly of the stirred autoclave. The temperature of the waste sample in the autoclave was continuously monitored by thermocouples which were positioned within the autoclave thermowells. In the wet air oxidation test, the autoclave was maintained at the desired temperature for the required length of time. After the desired temperature and time conditions had been satisfied, the autoclaves were cooled either by quenching the shaking autoclaves with tap water or by initiating cold water flow to the cooling coils of the stirred autoclaves. After cooling, the autoclaves were depressurized and the effluent streams were removed for subsequent analysis.

Wet Air Oxidation of Heavy Oil, Wellhead Oil, and Produced Water

The characteristics of the heavy oil, the wellhead oil, and the produced water are shown in Table 1. All three substances are products from a heavy oil production well in Canada.

The wellhead oil was mixed with produced water and oxidized at temperatures of 250, 280, and 300°C. All oxidations were conducted in a stirred autoclave using a given weight of oil, a given volume of produced water and a one (1) hour time at temperature. The results of these oxidations are reported in Table 2. The data indicate, as expected, an increasing utilization of the autoclave oxygen demand (AOD) with increasing temperature. AOD utilizations of 71.4, 86.4, and 88.0 percent are shown, respectively, for wet air oxidation temperatures of 250, 280, and 300°C. These AOD utilizations are graphically displayed in Figure 2. A visual inspection of the oxidized samples indicated that little if any imiscible oil was detected in the oxidized effluents. These results show that wet air oxidation can be used to dispose of oils that are dispersed in water. The implication that some of the energy released in the wet air oxidation reaction could be recovered is also an important conclusion.

Several series of wet air oxidations were conducted on mixtures of heavy oil and produced water. The purpose of these oxidation runs was to investigate the rate of heavy oil oxidation at various temperatures. A series of batch oxidations was conducted at 280, 300, and 320°C using reaction times of 0 to 240 minutes. All oxidations were conducted in shaking autoclaves. The results of these oxidations are reported in Tables 3, 4 and 5. These results show that a large fraction of the autoclave oxygen demand is exerted within the first 30 to 45 minutes of oxidation. However, the remaining autoclave oxygen demand is then slowly exerted out to 240 minutes and is only completely exerted after oxidation for 120 minutes at 320°C. Plots of the percent AOD exerted as a function of time, for the three oxidation temperatures, are shown in Figure 3. The slopes of the plots at zero time are not indicative of the actual rate of reaction due to the initiation and continuation of reaction during the heat-up period.

Wet Air Oxidation of Refinery Sludges

Various sludges are generated during the treatment of produced water. Generally, an oily sludge is generated in the initial oil-water separation that is usually effected in an API separator. If some form of biological treatment is applied to the remaining water portion of the produced water, a biological sludge is then generated. The characteristics of these two types of sludges are shown in Table 6. The API separator sludge is characterized by a high oil and grease content, 38.3% g/l, and a high Chemical Oxygen Demand (COD), 16.4%.

A feed material was prepared by combining oily sludge, biological sludge, and produced water in a 1:1:2 weight ratio. The resulting sludge was then oxidized in a shaking autoclave at temperatures of 240 and 280°C, using a 60 minute time at temperature. The chemical analyses of the feed sludge and the oxidized products are shown in Table 7. The analyses of the oxidized products indicate that COD reductions of 59.2 and 84.1 were achieved at wet air oxidation temperatures of 240 and 280°C, respectively. In addition, the oily nature of the feed was completely eliminated as was evident by the absence of any immiscible oil in the wet air oxidized effluents. The oil and grease analyses confirm the visual examination, indicating reductions of 93.6 and 99.1 percent at oxidation temperatures of 240 and 280°C, respectively.

A further analysis of the oxidized products indicates that the suspended solids remaining after wet air oxidation are comprised of inert solids, 84.9 and 90.2 percent ash, at 240 and 280°C, respectively. Finally, the BOD values for the oxidized effluents indicate that the remaining organic components are readily biodegradable and could be treated in the same biological system that was used to treat the produced water.

An oil refinery sludge which had accumulated over a number of years from a number of refining processes was oxidized at 240 and 280°C, using a time at temperature of 60 minutes. The untreated sludge was characterized by a high COD value, 717 g/l, and a high oil and grease content, 261 g/l. The refinery sludge required dilution with approximately 12 volumes of water for preparation of the feed mixture. The analyses of the untreated sludge, the diluted feed for wet air oxidation testing, and the oxidized products are reported in Table 8. The oxidized products again showed high levels of reduction of oil and grease, 95.6 and 99.9 percent at temperatures of 240 and 280°C, respectively.

Wet Air Oxidation of Spent Drilling Mud

A sample of spent drilling mud, which was taken from a storage lagoon, was subjected to wet air oxidation to improve the dewaterability of this material. The material as received was a concentrated mud, having a suspended solids concentration of approximately 500 g/l. This original drilling mud contained emulsifying agents and oils which inhibited good dewaterability. The drilling mud was diluted with tap water to a pumpable consistence. the diluted mud was neutralized to a pH of 7.1 and then oxidized in shaking autoclaves at 187°C for 30 minutes and at 240°C for 60 minutes. The analyses of the diluted feed and oxidized samples are shown in Table 9. These data indicate that a COD reduction of 45.3 and 63.8 percent was effected at temperatures of 187 and 240°C, respectively. The wet air oxidation effluents were readily dewaterable, having specific filtration resistance values of 18 and 17 (X 10^{-7} cm^{2}/g) for oxidiations at 187 and 240°C, respectively. The reported cake solids of 36.1 and 49.3 percent were obtained on cakes from the Buchner funnel specific filtration resistance test. Higher filter cake solids content could be obtained using a pressure filter.

The filter cake samples were subjected to the RCRA Extraction Procedure Toxicity Test for leaching metals. The results of these leachable metals tests are reported in Table 9. These data indicate that the concentrations of the leached metals are significantly below the allowable threshold concentrations. This would imply that the dewatered filter cakes will not pose an environmental risk when deposited in a landfill system.

Conclusions

The application of wet air oxidation has been tested on a variety of oils, oily sludges, and oily drilling muds. The results of these tests confirm that wet air oxidation can be used to dispose of waste oils and oily sludges. Wet air oxidation can also be used to improve the dewaterability of waste drilling muds which contain emulsifying agents and oils.

Literature Cited

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2. Hurwitz, E.G., Teletzke, G.H., and Gitchel, W.B., "Wet Oxidation of Sewage Sludge", Water and Sewerage Works 112, 298 (1965).

3. Teletzke, G.H., "Wet Air Oxidaiton", Chemical Engineering Prog. 60, 1, 33 (1964).

4. Canney, P.J. and Schaefer, P.T., "Detoxification of Hazardous Industrial Wastewaters by Wet Air Oxidation", 1983 Spring National AIChE Meeting, Houston, Texas, March 27-31, 1983.

5. Dietrich, M.J., Randall, T.L. and Canney, P.J. "Wet Air Oxidation of Hazardous Organics in Wastewater", Environmental Progress 4, 171 (1985).

FIGURE 1

WET OXIDATION FLOW DIAGRAM

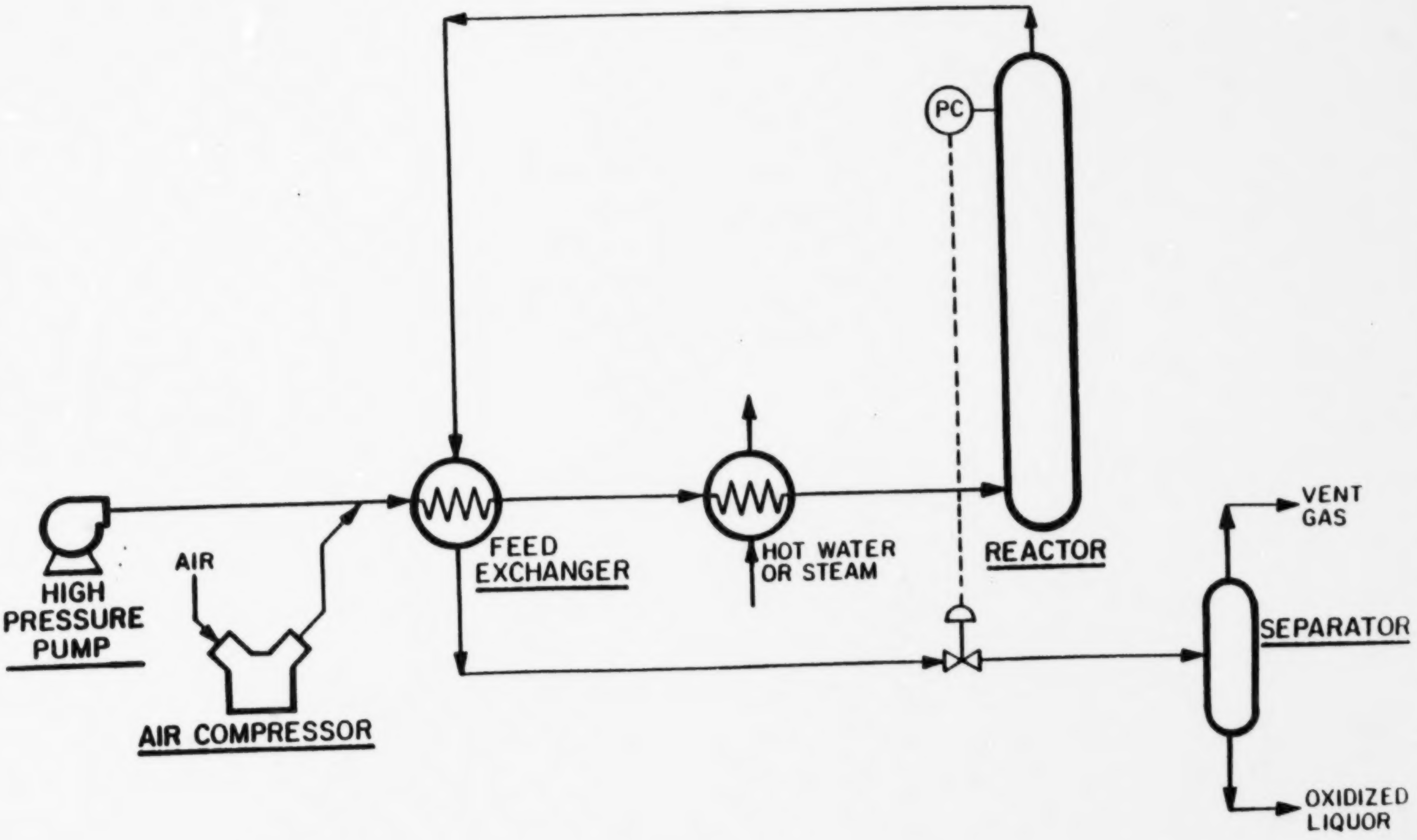
HIGH PRESSURE PUMP
AIR
AIR COMPRESSOR
FEED EXCHANGER
HOT WATER OR STEAM
PC
REACTOR
VENT GAS
SEPARATOR
OXIDIZED LIQUOR

FIGURE 2: WET AIR OXIDATION of WELLHEAD OIL with PRODUCED WATER

% AOD EXERTED vs. OXIDATION TEMPERATURE

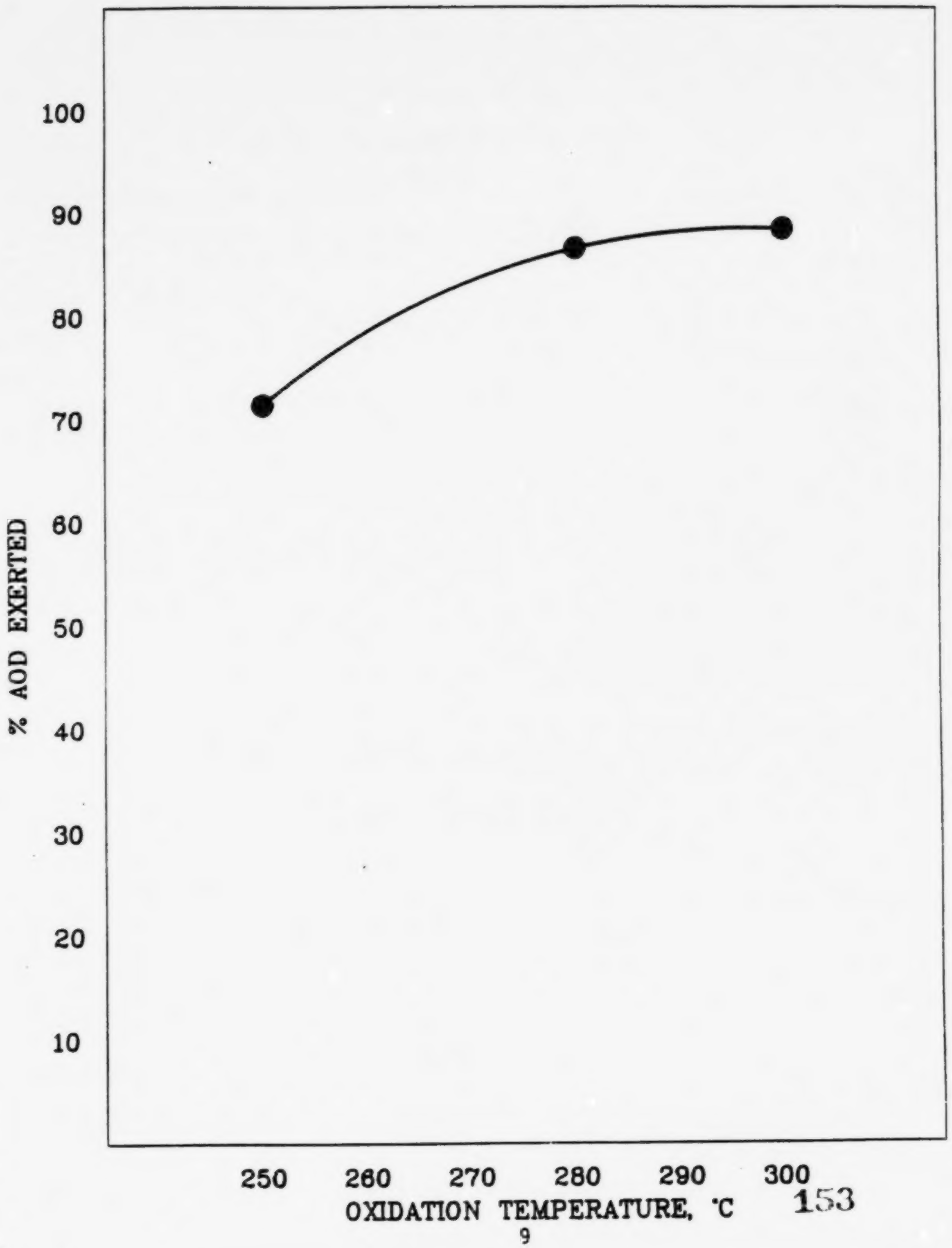

FIGURE 3: WET AIR OXIDATION of HEAVY OIL

BATCH RATE STUDIES

% AOD EXERTED vs. TIME at TEMP.

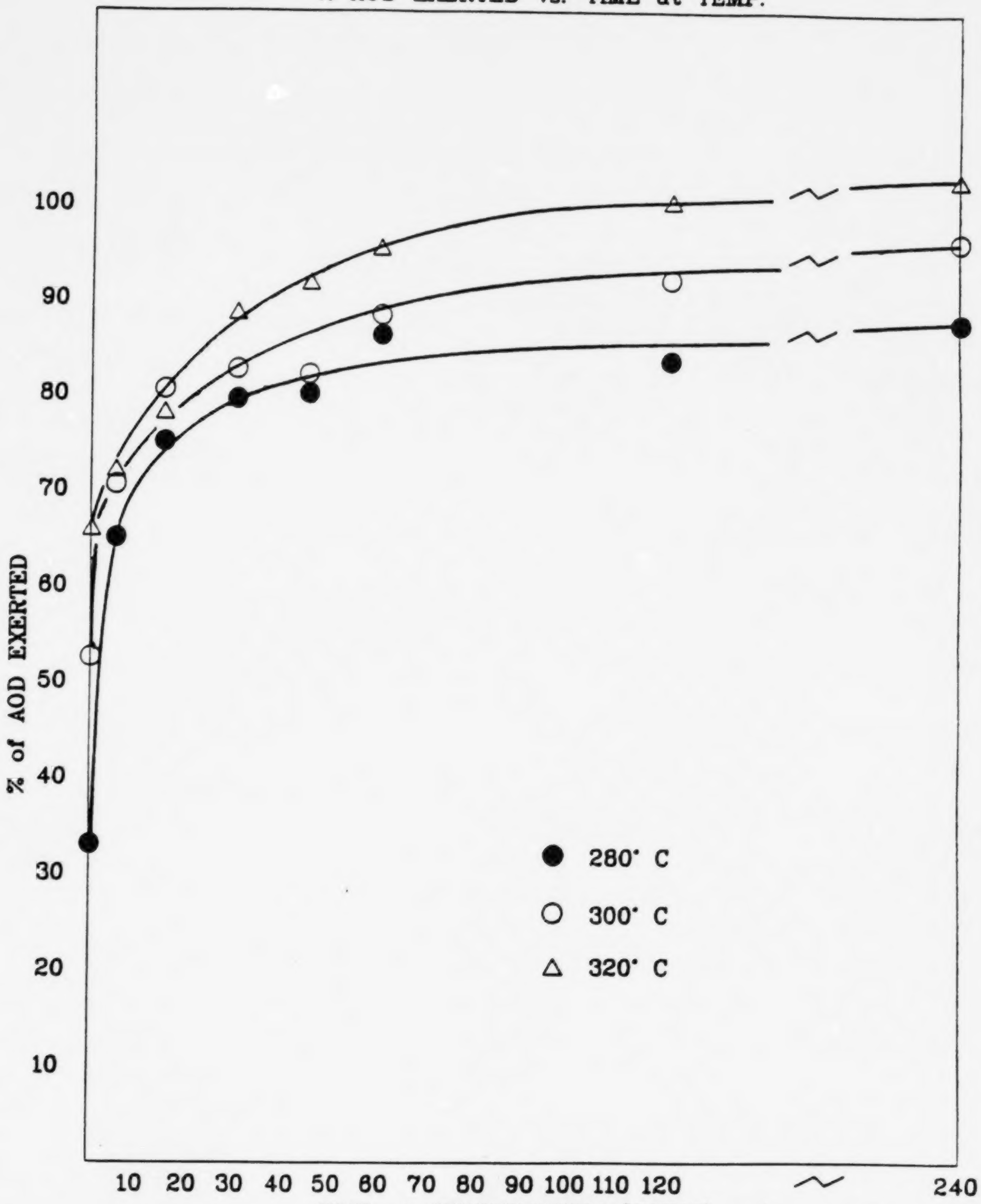

Table 1

Characterization of Produced Water, Wellhead Oil, and Heavy Oil

Sample	Produced Water	Wellhead Oil	Heavy Oil
Specific Gravity	0.999	1.020	1.018
COD	1.86 g/l	-	2.01 g/l
AOD	-	2.07 g/l	2.74 g/l
Total Solids	4.0 g/l	-	-
Total Ash	3.6 g/l	0.21%	0.12%
Water	-	0.22 g/g	0.01 g/g
Heat of Combustion	-	14134 BTU/lb	-

Table 2

Wet Air Oxidation of Wellhead Oil with Produced Water

Oxidation Temperature, °C	250	280	300
Time at Temperature, Min.	60	60	60
Input, Per Liter Slurry			
Wellhead Oil, g/l	24.2	24.2	24.2
Produced Water, ml/l	980	980	980
AOD, g/l	50.0	50.0	50.0
Total Solids, g/l	28.1	28.1	28.1
Total Ash, g/l	3.5	3.5	3.5
Volatile Solids, g/l	24.6	24.6	24.6
Oxidized Product			
Oxygen Uptake, g/l	35.7	43.2	44.0
COD, g/l	10.3	7.1	6.1
Total Solids, g/l	6.4	6.5	6.1
Total Ash, g/l	3.6	3.6	3.9
Volatile Solids, g/l	2.8	2.9	2.2
pH	1.8	1.8	1.8
% AOD Exerted	71.4	86.4	88.0

Table 3

Wet Air Oxidation of Final Heavy Oil with Produced Water

Oxidation Temperature, °C	280							
Time at Temperature, Min.	0	5	15	30	45	60	120	240
Input, Per Liter Produced Water								
Final Heavy Oil, g/l	20.1	20.2	20.1	20.1	20.0	20.1	20.2	20.1
AOD, g/l	55.1	55.3	55.1	55.1	54.8	55.1	55.3	55.1
Oxidized Product								
Oxygen Uptake, g/l	17.3	36.2	41.4	43.8	43.8	47.4	46.2	48.4
% AOD Used	31.4	65.4	75.1	79.5	79.9	86.1	84.0	87.9
Visible Residual Oil	Large	Small	Small	Small	Small	Trace	None	None

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Table 4

Wet Air Oxidation of Final Heavy Oil with Produced Water

Oxidation Temperature, ^{o}C	300							
Time at Temperature, Min.	0	5	15	30	45	60	120	240
Input, Per Liter Produced Water								
Final Heavy Oil, g/l	20.0	20.2	20.0	20.1	19.9	19.9	20.0	19.9
AOD, g/l	54.8	55.3	54.8	55.1	54.5	54.5	54.8	54.5
Oxidized Product								
Oxygen Uptake, g/l	27.8	38.8	44.0	45.0	44.2	47.7	50.4	52.7
% AOD Used	50.7	70.1	80.3	81.7	81.1	87.3	92.0	96.8
Visible Residual Oil	Large	Large	Small	Small	Trace	Trace	Trace	None

Table 5

Wet Air Oxidation of Final Heavy Oil with Produced Water

Oxidation Temperature, °C	320							
Time at Temperature, Min.	0	5	15	30	45	60	120	240
Input, Per Liter Produced Water								
Final Heavy Oil, g/l	19.9	20.1	20.1	20.0	19.9	20.0	19.9	19.9
AOD, g/l	54.5	55.1	55.1	54.8	54.5	54.8	54.5	54.5
Oxidized Product								
Oxygen Uptake, g/l	35.6	39.0	42.8	48.6	49.9	52.2	54.3	56.1
% AOD Used	65.4	70.8	77.7	88.7	91.6	95.3	99.7	103.0
Visible Residual Oil	Large	Large	Small	Trace	Trace	None	None	None

Table 6

Waste Characterization of Sludges from the Treatment of Produced Water

Waste Description	Bio Sludge(1)	Oily Sludge(2)	Produced Water
COD, g/l	15.1(%)	16.4(%)	9.3
BOD, mg/l	-	-	4294
Total Solids, g/l	11.3(%)	12.1(%)	34.7
Total Ash, g/l	13.9(%)	61.9(%)	30.1
Oil & Grease, g/l	-	38.3	1.7
pH	-	7.9	8.3

1. Biological Sludge from the treatment of produced water by the activated sludge process

2. Oily sludge from the API Separator

Table 7

Wet Air Oxidation of Oily Wastes
Generated from Produced Water

Sample Description	Diluted(1) Feed	Calculated(2) Composition	Oxidation Products	
Oxidation Temperature, °C	-	-	240	280
Time at Temperature, Min.	-	-	60	60
COD, g/l	45.3	83.4	18.5	7.2
COD Reduction, %	-	-	59.2	84.1
BOD, mg/l	-	-	7665	2518
NPOC, mg/l	2490	-	6210	1725
Oxygen Uptake, g/l	-	-	35.6	45.0
Total Solids, g/l	58.5	75.8	37.2	34.7
Total Ash, g/l	33.5	37.7	33.0	31.5
Suspended Solids, g/l	31.0	-	7.3	6.1
Suspended Ash, g/l	9.7	-	6.2	5.5
Suspended Volatile Solids, g/l	21.3	-	1.1	0.6
Suspended Volatile Solids Reduction, %	-	-	94.8	97.2
Oil & Grease, g/l	4.4	-	0.28	0.04
pH	6.9	-	6.2	7.0

(1) Composed of 500 g oily sludge, 500 g of biological sludge and 1000 g of produced water

(2) Calculated from Waste Characterization Analysis

Table 8

Wet Air Oxidation of Refinery Sludge

Sample Description	Refinery Sludge	Diluted Feed	Oxidized Product	
Oxidation Temperature, ^{o}C	-	-	280	240
Time at Temperature, Min.	-	-	60	60
AOD, g/l	717.2	58.5	-	-
O_2 Used, g/l	-	-	48.0	36.8
Percent Oxidation	-	-	82.1	62.9
COD, g/l	898.9	66.6	8.4	15.4
COD Reduction, %	-	-	87.4	76.9
Oil & Grease, mg/l	261,000	19,000	10	840
Oil & Grease Reduction, %	-	-	99.9	95.6
Total Solids, g/l	417.3	37.0	15.8	-
Total Ash, g/l	212.4	21.3	13.9	-
Total Volatile Solids, g/l	204.9	15.7	1.9	-
Total Volatile Solids Reduction, %	-	-	87.9	-
pH	-	-	3.4	3.2

Table 9

Wet Air Oxidation of Spent Drilling Mud

Drilling Mud	Diluted 4:1	Thermal Conditioning Products	
Processing Temperature, °C	-	187	240
Time at Temperature, Min	-	30	60
Analyses			
COD, Soluble, mg/l	5720	3130	2070
% COD Reduction	-	45.3	63.8
BOD, Soluble, mg/l	2625	1273	846
TOC, Soluble, mg/l	2010	1230	948
Total Solids, g/l	113.4	117.0	122.8
Ash, g/l	107.5	109.6	114.7
Suspended Solids, g/l	103.7	88.6	113.3
Suspended Ash, g/l	100.9	84.3	106.9
pH (Neutralized Feed)	7.1	6.7	6.8
Specific Filtration Resistance, $cm^2/g \times 10^{-7}$	155	18	17
Filter Cake Solids, %	-	36.1	49.3

Table 10

RCRA Metals Leached from Filter Cakes of Wet Air Oxidized Drilling Mud

Metal	Extraction Procedure EP Toxicity Threshold Concentration	Thermally Conditioned Solids	
		187°C/30 Min.	240°C/60 Min.
Arsenic	5.0	0.016	0.013
Barium	100.0	0.073	0.052
Cadmium	1.0	0.008	0.009
Chromium	5.0	0.009	0.009
Lead	5.0	0.260	0.123
Mercury	0.2	0.000	0.001
Selenium	1.0	0.004	0.004
Silver	5.0	0.005	0.005

* All values in mg/l

THE B.E.S.T.$^{\mathrm{TM}}$ PROCESS

AN INNOVATIVE AND DEMONSTRATED PROCESS FOR TREATING HAZARDOUS SLUDGES AND CONTAMINATED SOILS

by

DOUGLAS A. AUSTIN
RESOURCES CONSERVATION CO.
SEATTLE, WASHINGTON

ABSTRACT

For many industries and at many industrial and Superfund hazardous waste sites the tasks of waste management and cleanup are complicated by large volumes of difficult to handle sludges and contaminated soils. A steadily growing number of innovative and alternative technologies have been proposed for the treatment of these materials, but most are still in the pilot scale or demonstration stage. Few have reached or are near commercial application. An exception is the B.E.S.T.$^{\mathrm{tm}}$ process, developed and patented by Resources Conservation Co. (RCC). The B.E.S.T.$^{\mathrm{tm}}$ process reached prototype status in the mid-1970s. And a full scale, transportable B.E.S.T.$^{\mathrm{tm}}$ unit recently completed the clean up of 3700 yd^3 of acidic, oily, PCB-contaminated sludges at a Superfund site in Georgia, the first such use of an "innovative and alternative" technology.

The B.E.S.T.$^{\mathrm{tm}}$ process employs the inverse miscibility properties of aliphatic amines to break down suspensions and emulsions in sludges and contaminated soils. This enhances the separation of these materials into distinct fractions; disposable water, reuseable oil/hydrocarbon, and dry solids. This opens up a wider range of reuse and disposal options. As a final solution for hazardous waste management, B.E.S.T.$^{\mathrm{tm}}$ process treatment costs have been demonstrated to be lower than incineration or commercial landfilling. In most cases the composition of residual solids is similar to that of incinerator ash. The closed nature of the process makes it virtually free of air emissions.

The B.E.S.T.$^{\mathrm{tm}}$ process has application processing oily sludges and contaminated soils from refineries, petrochemical plants, wood treating operations, wastewater treatment systems, steel mills and similar facilities. It is also being developed for the removal of PCBs from soils and sediments.

INTRODUCTION

SARA (Superfund Amendments and Reauthorization Act) mandates the use of final solutions for Superfund site cleanups whenever feasible. RCRA (Resource Conservation and Recovery Act), following reauthorization in 1984, has to be interpreted as at least strongly encouraging final solutions for industrial hazardous waste management. This is consistent with growing public and regulatory pressure against cleanup methods which merely move wastes from one place to another, or treat them in such a way that a new problem is created.

Land filling and encapsulation methods accomplish little except to delay a final solution. The most sophisticated of fixation technologies may also cause an even larger disposal later. Incineration can be prohibitively expensive and has poor public image due to the potential for air emissions.

These issues serve to underscore the growing need for hazardous waste treatment technologies which can work toward a final solution, but which have reasonable costs and minimum adverse environmental impact. The B.E.S.T.^{tm} process is such a technology.

ALIPHATIC AMINES

The unusual inverse miscibility properties of aliphatic amines have been a subject of curiosity for chemists and chemical engineers for many years. Figure 1 illustrates that property for one of these chemicals. At low temperatures (<20^{o}C) water and amine are totally miscible. At higher temperatures, separation into two phases is rapid and fairly complete. Residual amine in the water phase and water in the amine phase is only a few percent. Most of these amines are excellent solvents for a wide variety of hydrocarbons. These properties remained a mere curiosity until the mid-1970s, when RCC process engineers incorporated them in a process for dewatering and de-oiling sludges.

An additional aspect of the amines being employed by RCC in the B.E.S.T.^{tm} process is that they are not regulated as toxic, hazardous chemicals under TSCA and RCRA. Many of them, however, have physical properties which require careful handling and process design. These properties include flammability and an ammonia-like odor.

THE B.E.S.T.^{tm} PROCESS

The B.E.S.T.^{tm} process is usually categorized as a solvent extraction processes by engineers, regulators, and others. That categorization is essentially correct, but there is an important distinction between the B.E.S.T.^{tm} process and other extraction processes which employ solvents. That is that most solvent-based process are focused on the separation of oil and other hydrocarbons from waste. Water is secondary, or even an impediment. In B.E.S.T.^{tm} the opposite is the case. Both water and oil are primary targets.

Figure 2 schematically illustrates the two stages of the B.E.S.T.^{tm} process; the 'cold stage', and the 'hot stage'. In the cold stage sludges or soils are mixed with amine at low temperature (<20^{o}C). Mixture ratio is a function of feed composition, but is often on the order of two parts amine for each part of sludge. At this temperature water and hydrocarbons are soluble in the amine. Suspensions and emulsions are virtually eliminated. The solids fraction becomes readily separated by settling or or other physical means and dried. Since the amine is alkaline (pH~10), heavy metals in the waste are converted to hydrated oxides, which precipitate and exit the process with the solids fraction.

To begin the 'hot stage' the single phase amine/water/oil fraction is heated to a temperature above the miscibility line (>20^{o}C). Two distinct phases form after heating; amine/oil, and water. These phases can then be separated by decanting. The final steps in this process involve solvent recovery, which is generally accomplished by thermal means. Triethylamine has relatively modest heat of vaporization (133 BTU/lb) and water azeotrope boiling point (172^{o}F), so recovery is not energy intensive.

Figure 3 is a process flow diagram for a continuous flow B.E.S.T.^{tm} process. It illustrates one way to assemble individual process elements to accomplish the separation described above. This configuration was employed by RCC in a 70 ton/day system (wet feed capacity) which was constructed by RCC and used by EPA during a 1987 removal action at a CERCLA site in Georgia. In this configuration the process is employed primarily for pumpable materials, such as sludges. Modifications to the front end of the process facilitate the treatment of soils. Figure 4 is a photograph of this system at the site.

Sludge is introduced to a mix tank and combined with refrigerated solvent. The solvent has been chilled sufficiently that the resulting temperature is below the miscibility line (<20^{O}C in Figure 1). Sufficient residence time is provided to permit complete solvation and formation of a single liquid phase. Solids are separated from the liquid by centrifugation. Centrifugation accelerates solids separation and helps insure a high capture rate for submicron size particles.

A second solids washing step is employed for high oil sludges (>10% oil) if it is necessary to ensure the product solids contain less than 1% (wt) residual oil and grease. Additional washing steps may be employed if even lower oil concentration in the solids is necessary. Solids cake from the final extraction step goes to a closed, indirectly heated dryer. Vaporized solvent is drawn off the dryer, condensed, and reused in the process. Dried solids typically contain >99% solid matter.

Liquid from the first mixing step is heated and introduced to a decanter vessel. Sufficient residence time is provided in the decanter to ensure complete separation into amine/oil and water phases. The amine/oil phase is drawn off the top of the decanter and pumped to an amine recovery system. This system may consist of an amine evaporator or an evaporator combined with a finishing distillation column. Recovered solvent is condensed and reused. Since the oil in the column bottoms is chemically unaltered by the B.E.S.T.^{tm} process, and is in a sense purified, it may have significant value.

Water phase is drawn off the bottom of the decanter and pumped to a stripping column for recovery of remaining solvent (2-3%).

The B.E.S.T.^{tm} process operates at or near ambient pressure, over a moderate range of temperatures, and at a mildly alkaline pH. These conditions obviate the necessity for special materials of construction, pressure vessels, or extraordinary heat conservation methods. Since the process is a closed loop, with one small non-condensible vent, there are virtually no air emissions.

PROCESS APPLICATION

The B.E.S.T.^{tm} process was developed by RCC to commercial status during the mid-1970s. At that time hazardous waste management was a topic of discussion, but not so much one of legislation. RCC's focus was on the dewatering of municipal water treatment sludges. The process was successfully demonstrated several times and its ability to consistently produce dry, oil-free solids was confirmed. However, the availability of low cost land treatment alternatives and declining regulatory pressure limited opportunities for the process. Tests during this period showing the process' ability to break difficult hydrocarbon emulsions, but there was little incentive at that time to develop this feature.

Development of the B.E.S.T.^{tm} process began anew in 1985 following the reauthorization of the Resources Conservation and Recovery Act (RCRA). Laboratory work by RCC analytical chemists illustrated the ability of the B.E.S.T.^{tm} process to separate RCRA-listed oily sludges (e.g. K051 API Bottoms) into three fractions; treatable water, reuseable oil, and dry solids. Further investigation showed that in most cases the product solids would be a candidate for RCRA delisting. Economic projections indicated that in all applications the B.E.S.T.^{tm} process would be more economical than incineration. But real encouragement came from the discovery that in many instances the B.E.S.T.^{tm} process is more cost effective than regulated land application.

During the last two years RCC's analytical laboratory has evaluated more than 150 different oily sludges and contaminated soils. We do not yet know the full range of application of the process, but we have identified a number of applications for which B.E.S.T.^{tm} process economics and performance are very good. Figure 5 lists some of these applications.

B.E.S.T.^{tm} PROCESS PERFORMANCE

During early 1985 RCC obtained samples of RCRA-listed hazardous sludges from several oil refineries. Samples included API Bottoms, DAF Float, Slop Oil Emulsion Solids, etc. These materials provided a good base for understanding the performance of the B.E.S.T.^{tm} process when applied to oily sludges and contaminated soils. Figure 6 illustrates typical results obtained during bench scale simulation of the B.E.S.T.^{tm} process on a sample of API Bottoms (RCRA K051) from a large Gulf Coast refinery.

These results led to the following observations and conclusions:

1) The water fraction from B.E.S.T.^{tm} treatment could be discharged through a refinery wastewater treatment system.

2) The oil fraction recovered by B.E.S.T.^{tm} treatment could be recycled to refinery processing units without further treatment.

3) The solids fraction from B.E.S.T.^{tm} treatment be a candidate for RCRA delisting.

These results and conclusions have since been confirmed numerous times on similar sludges from other facilities. A particularly significant reconfirmation of these conclusions occurred during a 1987 pilot scale test program conducted for the American Petroleum Institute.

B.E.S.T.^{tm} process economics vary widely from one application to another. Variables include feed composition (and variability), product requirements, utility costs and availability, feed flow rate and volume (if not a continuous flow), fixed costs (installation and demobilization), etc. The total cost range may vary as follows (wet feed basis):

Low	$50/ton	Owner operated on continuously generated, large volume, low organic sludge in a large, integrated industrial facility.
High	$150/ton	RCC owned and operated on a stand alone basis at a small, remote Superfund site.

OPERATIONAL EXPERIENCE

During 1985 RCC initiated the fast-track design and construction of a commercial scale B.E.S.T.^{tm} process unit configured specifically for oily sludges. The unit was configured to have a peak capacity of 100 tons/day of sludges containing up to 20% (wt) oil/organic and up to 20% (wt) solids. By early 1986 construction had been completed the unit was committed to the General Refining, Inc. CERCLA site near Savannah, GA.

The General Refining site is an abandoned oil reclamation and re-refining facility. Investigators found four unlined lagoons containing acidic ($pH<2$) oily sludges, piles of oily filter medium, and oil/water separator pits which had been backfilled with soil. Lead and other heavy metals were prevalent in all materials and low levels of PCBs (<10 mg/l) were found in most materials.

EPA determined that the removal of up to 10,000 yd^3 of material might be required to halt the migration of contaminants from the site. An investigation of process alternatives compared incineration (on-site and off-site), excavation and transportation to a commercial landfill, and on-site treatment by the B.E.S.T.^{tm} process. Decision criteria included economics, equipment availability and capacity, and performance. EPA chose the .S.T.^{tm} process as the most cost effective and suitable removal option for this site.

B.E.S.T.^{tm} process equipment was moved to the site and set up during 1986 (Figure 4). Processing of sludges and soils at the site proceeded through early 1987. Work was concluded in March when EPA determined that sufficient material had been removed. During its tenure at the General Refining, Inc. site the B.E.S.T.^{tm} system processed a total of 3700 tons of contaminated materials.

Composition of sludges and soils at the site varied widely from point to point laterally and vertically within the lagoons. Nominal composition was roughly 10% oil, 70% water, and 20% solids. But during actual operation oil ranged from 0-40%, solids from 2-30%, and water from 60-100%.

Product water from B.E.S.T.^{tm} treatment was carried by tanker to a nearby industrial wastewater treatment system and discharged. Recovered oil was heavy (API gravity _15) but was suitable for use as fuel. The B.E.S.T.^{tm} process isolated the PCBs in the oil fraction, but the average concentration was less than 50 mg/l. Therefore, the oil could be used by a fuels blender. Residual PCB levels in the solids fractions were not significant (_0.1 ppm) and were nondetectable in the water. Product solids were suitable for retention at the site and were placed back in the emptied lagoons.

Near the end of the treatment program at the General Refining site RCC and EPA cooperated in a comprehensive random sampling program. Over 160 samples of input and output streams were collected randomly during a 24 hour period with the B.E.S.T.^{tm} system operating at capacity. These samples were shipped to an EPA approved lab for analysis. Results are summarized in Figure 7.

This use of an 'innovative and alternative' technology at a Superfund site was not without its moments of frustration. Early on, mechanical problems were encountered with individual pieces of equipment and many hours were devoted to redesign and reconfiguration. Developing a front end materials handling system which could feed a relatively uniform feed composition to the B.E.S.T.^{tm} system was a challenge. Methods also had to be developed to handle the very dry, dusty, lead-bearing (2-3wt%) solids produced by the system.

On the other hand, there were notable successes. An automatic, programmed logic-type control system simplified start up, operation, and shut down operations. And most important of all, the process itself worked as projected from the very beginning. It produced oil, water, and solids products which met contractual requirements.

During the final months of the General Refining cleanup project early mechanical problems were resolved and the system operated around the clock. The unit has subsequently been demobilized from the site, has undergone modification and upgrading, and is awaiting shipment to its next job at a site in the Midwest.

PCB REMOVAL FROM SOILS AND SLUDGES

During the last six months RCC has been increasingly involved in studies with PCB-contaminated soils. The B.E.S.T.^{tm} process has shown an ability to remove 99+% of PCBs from a wide variety of sludges, soils, and sediments. A recent EPA-funded study of PCB treatment technologies ranked B.E.S.T.^{tm} #1 among technologies considered to be candidates for treating sediments from Superfund sites in the Hudson River and in New Bedford Harbor (MA)[1].

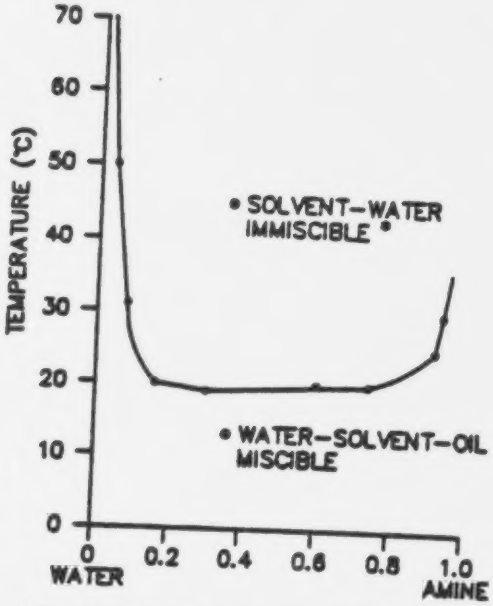
A recently presented paper[2] summarized RCC's experience with a variety of PCB bearing wastes. Data from that paper are reproduced here as Figure 8.

RCC is is developing a portable version of the process specifically for treating soils and sludges at remote sites. This system will have a feed capacity of 10-30 tons per day and will operate in a semi-batch mode rather than in continuous operation. Former transformer handling sites, natural gas pumping stations, and similar sites will be candidates for cleanup.

CONCLUSION

Land disposal is an increasingly uneconomic and counter-productive way to manage hazardous wastes. RCC's B.E.S.T.^{tm} process is now a proven technology and represents an early success in the drive to develop innovative and alternative technologies which can achieve the final solutions needed to eliminate hazardous materials from the environment.

References:
1 "PCB Sediment Decontamination Processes - Selection for Test and Evaluation", Ben Carpenter, Research Triangle Institute, 9-87.
2 "Removal of Polychlorinated Biphenyls (PCBs) from Sludges and Sediments with B.E.S.T.^{tm} Extraction Technology", Mark Tose, AIChE Annual Meeting, 11-87, New York City.



*OIL STAYS WITH SOLVENT DURING SEPARATION

FIGURE 1
TRIETHYLAMINE-WATER SOLUBILITY

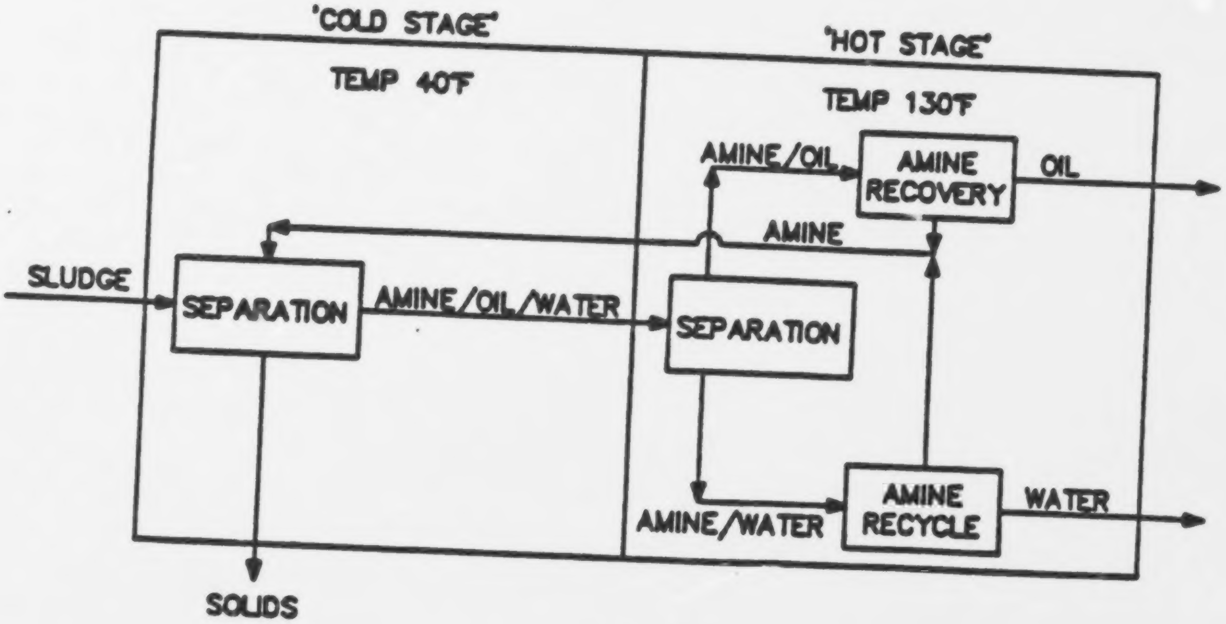

'COLD STAGE'
TEMP 40°F
'HOT STAGE'
TEMP 130°F
SLUDGE
SEPARATION
AMINE/OIL/WATER
SEPARATION
AMINE/OIL
AMINE RECOVERY
OIL
AMINE
AMINE/WATER
AMINE RECYCLE
WATER
SOLIDS

FIGURE 2
B.E.S.T.™ SEPARATION

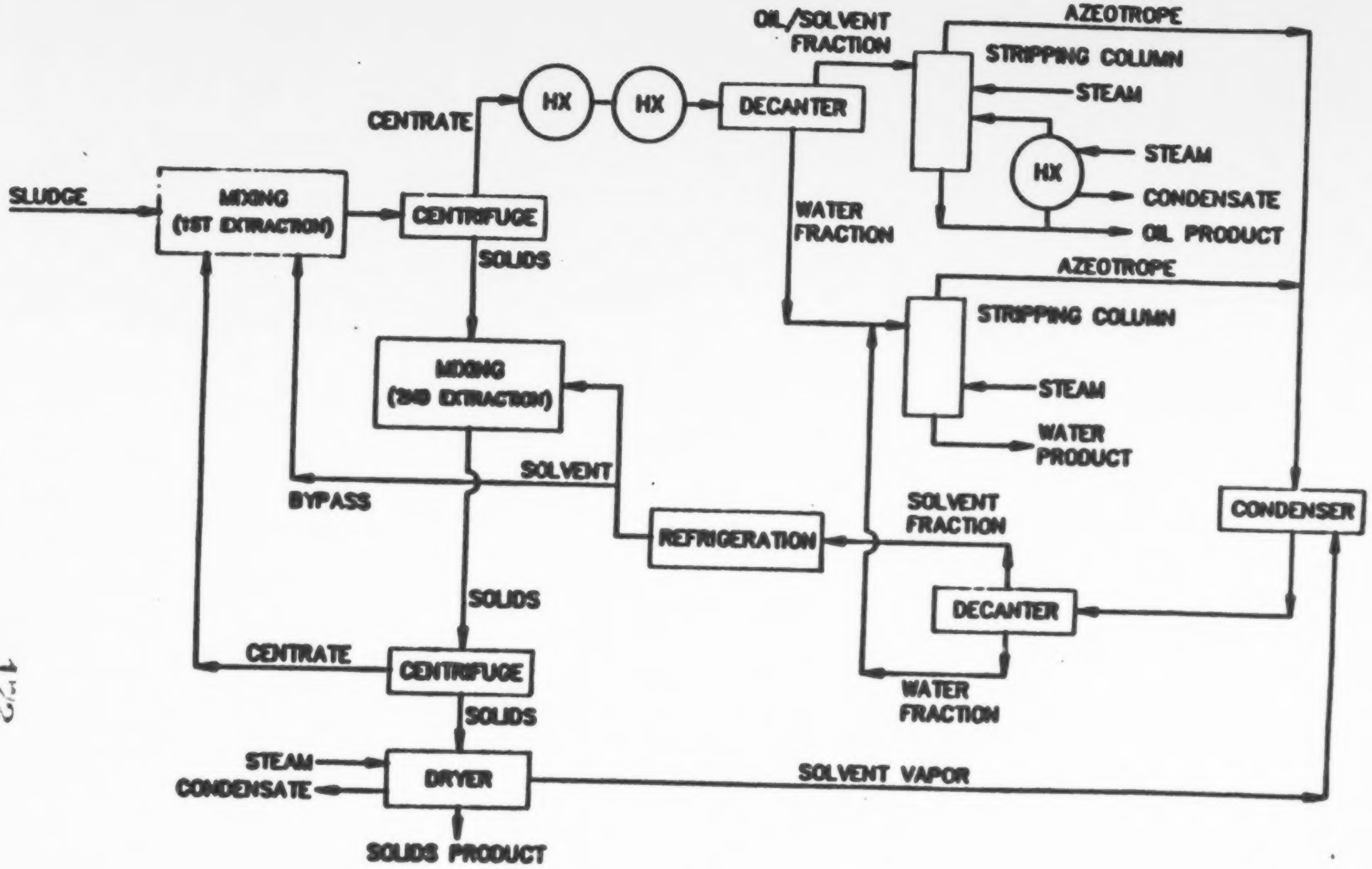

SLUDGE
MIXING (1ST EXTRACTION)
CENTRIFUGE
CENTRATE
SOLIDS
HX
HX
DECANTER
OIL/SOLVENT FRACTION
WATER FRACTION
AZEOTROPE
STRIPPING COLUMN
STEAM
HX
STEAM
CONDENSATE
OIL PRODUCT
AZEOTROPE
STRIPPING COLUMN
STEAM
WATER PRODUCT
MIXING (2ND EXTRACTION)
SOLVENT
BYPASS
REFRIGERATION
SOLVENT FRACTION
CONDENSER
DECANTER
WATER FRACTION
SOLIDS
CENTRATE
CENTRIFUGE
SOLIDS
STEAM
CONDENSATE
DRYER
SOLIDS PRODUCT
SOLVENT VAPOR

FIGURE 3
B.E.S.T.™ PROCESS FLOW DIAGRAM

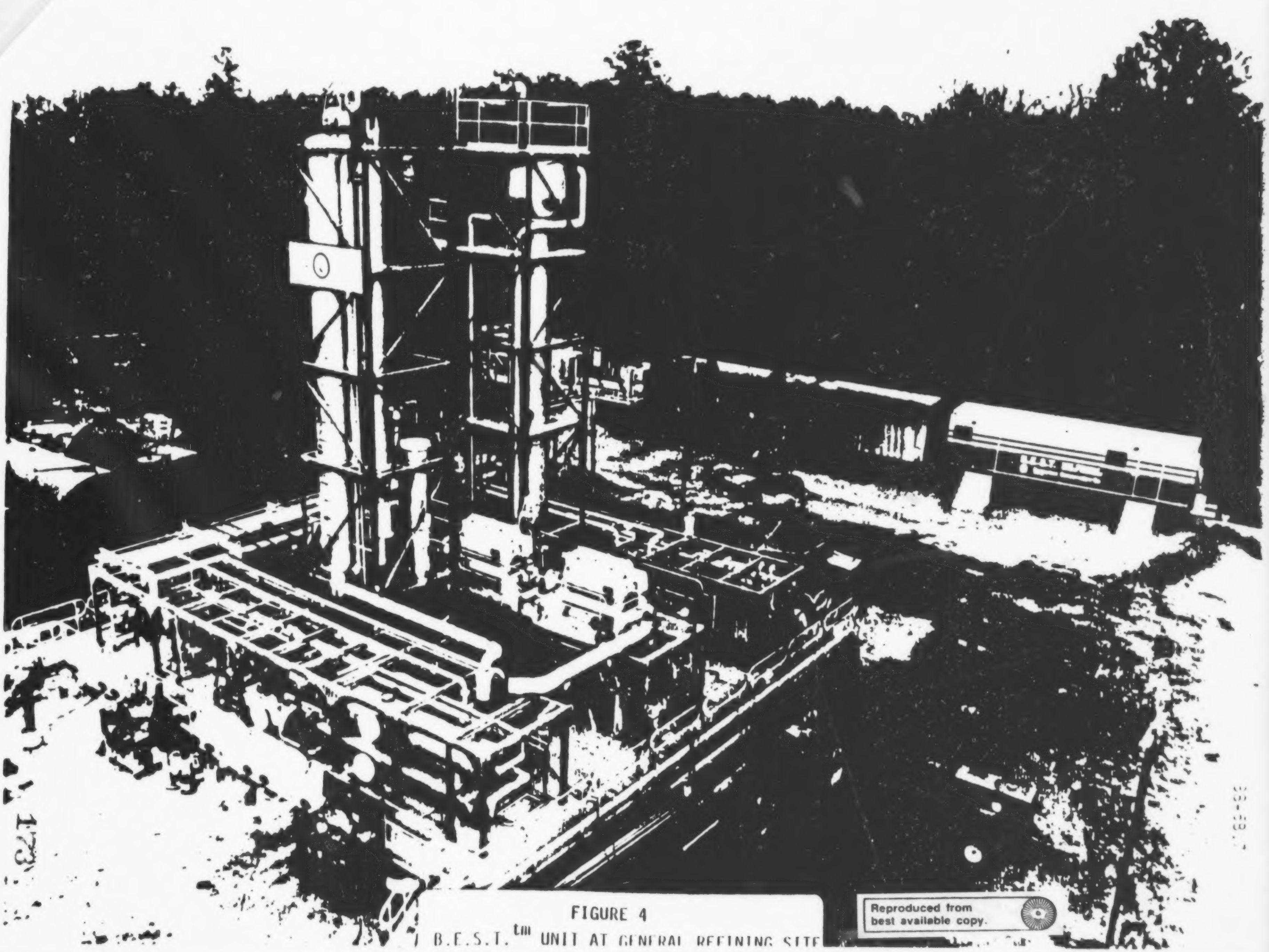


FIGURE 4

B.E.S.T.^{tm} UNIT AT GENERAL REFINING SITE

Reproduced from
best available copy.

RCRA–LISTED HAZARDOUS WASTE

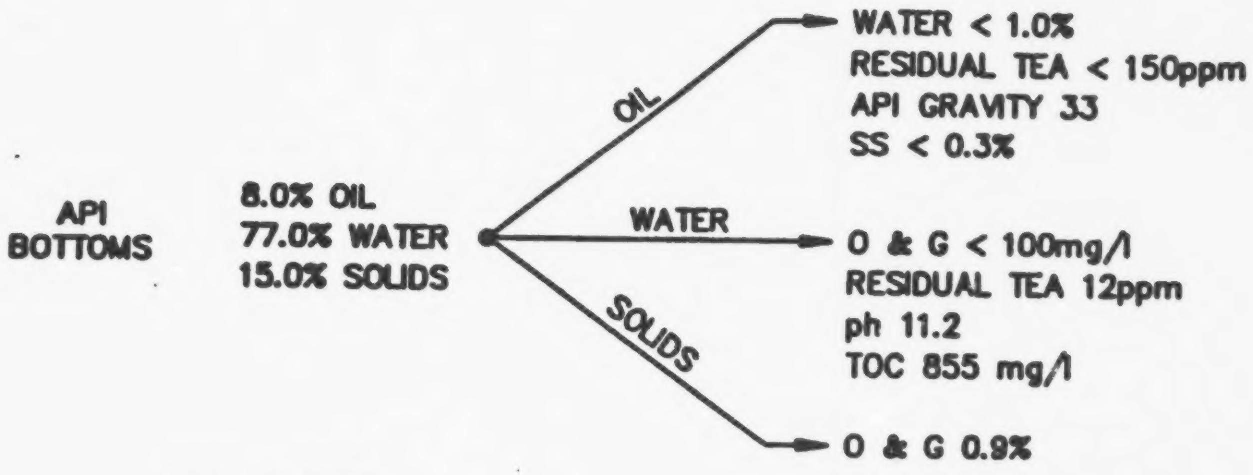
K001	CREOSOTE SLUDGES	K060	AMMONIA STILL SLUDGE
K048	DAF FLOAT	K089	DECANTER TAR SLUDGE
K049	SLOP OIL EMULSION SOLIDS	K084	PHARMACEUTICAL SLUDGE
K050	HEAT EXCHANGER SLUDGE	K101	DISTILLATION RESIDUES
K051	API BOTTOMS	K044	WATER TREATMENT SLUDGES
K052	LEADED TANK BOTTOMS		

OTHERS

PCB CONTAMINATED SLUDGES AND SOILS
STEEL MILL WASTEWATER TREATMENT SLUDGES
MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGES
OILY WASTE IMPOUNDMENTS
REFINERY ALKYLATION SLUDGES
BY–PRODUCT EMULSIONS FROM PETROLEUM REFINING OPERATIONS
PETROLEUM STORAGE TANK BOTTOMS

FIGURE 5

APPLICATIONS OF THE B.E.S.T.™ PROCESS

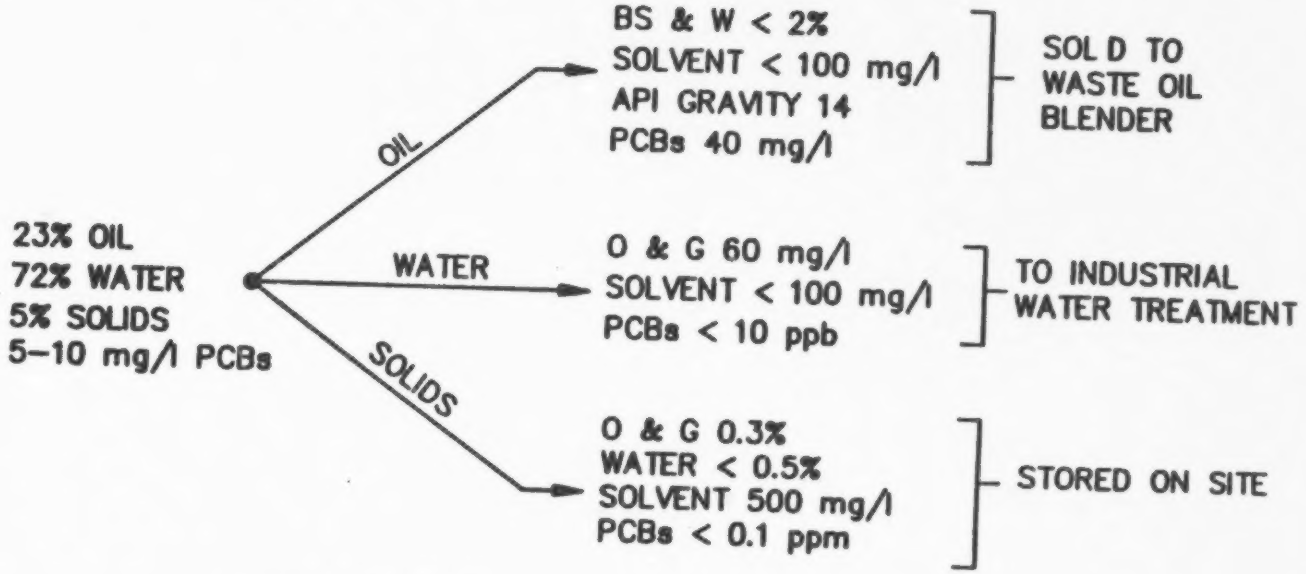

API
BOTTOMS
8.0% OIL
77.0% WATER
15.0% SOLIDS
OIL
WATER
SOLIDS
WATER < 1.0%
RESIDUAL TEA < 150ppm
API GRAVITY 33
SS < 0.3%
O & G < 100mg/l
RESIDUAL TEA 12ppm
ph 11.2
TOC 855 mg/l
O & G 0.9%

TOTAL METALS IN SOLIDS	
As	6.9
Ba	21.3
Cd	0.4
Cr	175
Pb	55
Zn	157
Se	58

TCLP METALS IN SOLIDS	
As	< .5
Ba	1.0
Cd	< .02
Cr	<0.1
Pb	<0.2
Hg	<0.1
Se	< .5
Ag	< .02

FIGURE 6

TYPICAL B.E.S.T.™ RESULTS
GULF COAST REFINERY


23% OIL
72% WATER
5% SOLIDS
5–10 mg/l PCBs
OIL
WATER
SOLIDS
BS & W < 2%
SOLVENT < 100 mg/l
API GRAVITY 14
PCBs 40 mg/l
SOL D TO WASTE OIL BLENDER
O & G 60 mg/l
SOLVENT < 100 mg/l
PCBs < 10 ppb
TO INDUSTRIAL WATER TREATMENT
O & G 0.3%
WATER < 0.5%
SOLVENT 500 mg/l
PCBs < 0.1 ppm
STORED ON SITE

PRODUCT SOLIDS

TOTAL METALS

As	< 5.0 ppm
Ba	410
Cd	3.4
Cr	21
Pb	23,000
Zn	1000
Se	< 5.0

TCLP METALS

As	< 0.03 ppm
Ba	< 0.03
Cd	--
Cr	< 0.05
Pb	5.2
Hg	< 0.001
Se	0.008
Ag	--

FIGURE 7

TYPICAL B.E.S.T.™ RESULTS

PCB Concentration in Glassware B.E.S.T.^{TM} Workups
(ppm unless otherwise noted)

Client	Type of Sample	Initial Concentration (Wet)	Initial Concentration (Dry)	Product Fraction Concentrations Solids	Product Fraction Concentrations Oil	Product Fraction Concentrations Raw Water	%Extraction Efficiency (Dry Basis)	Extraction Steps
A.	Soil	1,500.	1,685.	19.	600,000.	N/A	98.9	6
B.	Spiked Sediment	124.		.082	N/A	N/A	99.9	6 hour Soxhlet
C.	Oily Sludge	1,300.	7,065.	47.	365,000.	1.6	99.3	2
D.	Oily Sludge	106.	189.3	.75	270.	N/A	99.6	2
E.	Oily Sludge (A)	51.	71.	2.7	80.	N/A	96.2	3
	Oily Sludge (B)	21.	27.	.30	71.	N/A	98.9	2
	Oily Sludge (C)	11.	13.	.06	52.	N/A	99.5	3
F.	Sediment (A)	22.	41.	1.9	5,300.	<.02	95.4	2
	Sediment (B)*	960.	1,157.	40.	N/A	N/A	96.5	5
G.	Oily Sludge (A)	68.	170.	1.1	190.	N/a	99.4	2
	Oily Sludge (B)	83.	138.	1.1	N/A	N/A	99.2	2
	Oily Sludge (C)	N/A	N/A	1.8	N/A	N/A	N/A	2

* 10% Hexane in TEA

FIGURE 8

PCB CONCENTRATION IN B.E.S.T.^{TM} GLASSWARE WORKUPS

PERSPECTIVES/TRENDS IN USED OIL MANAGEMENT

by

Dennis W. Brinkman
IITRI/National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005
918/336-2400

INTRODUCTION

Most of the 750-million gallons of waste oils collected each year in the U.S. is reprocessed to some degree and sold as fuel. The fuels derived from these wastes contain higher levels of contaminants (including toxic metals, such as lead) than is typical of virgin fuel oils. Furthermore, it is common to find high levels of halogenated compounds in oily wastes collected for recycling. These organohalogens are typically chlorine-containing solvents used for cleaning purposes by many garages, service stations, and other industries (1).

There is general consensus that proper management can control potential problems associated with the disposal/recycling of used oil. Past experience, however, shows that without enforced regulation, blatant and irresponsible disposal practices can result. Notable examples include the use of used oils contaminated with dioxin wastes as dust suppressants on public roads and the use of contaminated waste-derived fuels in apartment building furnaces. The classic example is the storm sewer disposal practice by most weekend mechanics making do-it-yourself automobile crankcase oil changes. This small-scale pollution, while significant in the aggregate, can never be regulated, so will have to be addressed through education.

To demonstrate the complexity of used oils, table 1 contains a listing of the used oils listed as hazardous waste in New Jersey. Table 2 provides an example of allowable levels of specified constituents if the oil is to be burned as a non-hazardous waste fuel. Regulations that establish allowable concentrations of hazardous components including metals, halogens, and PCB's in waste-derived fuels can create as well as solve problems, however. Such specifications almost invariably necessitate major changes in collection, handling, reprocessing, and disposal procedures being used by the industry. If not carefully formulated and implemented, these changes can be so complex or cost-intensive that they destroy the competitive marketability of fuels derived from wastes.

TABLE 1. - Used oil listed as hazardous wastes in New Jersey

N.J. Hazardous Waste Number	Waste Description
X721	Waste automotive crankcase and lubricating oils from automotive service and gasoline stations, truck terminals and garages
X722	Waste oil and bottom sludge generated from tank cleanouts from residential/commercial fuel oil tanks
X723	Waste oils and bottom sludge generated by gasoline stations when gasoline and oil tanks are tested, cleaned, or replaced
X724	Waste petroleum oil generated when tank trucks are cleaned
X725	Oil spill cleanup residue which: A) is contaminated beyond saturation, or B) the generator fails to demonstrate that the spilled material was not one of the listed hazardous waste oils
X726	The following used and unused waste oils, metal working oils, turbine lubricating oils, diesel lubricating oils, and quenching oils
X727	Waste oils from the draining, cleaning, or disposal of electric transformers
X728	Bottom sludge generated from the processing, blending, and treatment of waste oil in waste oil processing facilities

TABLE 2. - New Jersey liquid fuel standards

Constituents/Property	Allowable
BS&W, vol pct	2.0 max
Ash, wt pct	0.2 max
PCB's, ppmw	5.0 max
Sulfur, wt pct	0.3 max
Nitrogen, wt pct	0.8 max
Total halogens, ppmw	1,000. max[1]
Arsenic, ppmw	5. max[2]
Beryllium, ppmw	0.5 max[2]
Cadmium, ppmw	2. max[2]
Chromium, ppmw	10. max[2]
Lead, ppmw	25. max[2]
Mercury, ppmw	0.1 max[2]
Nickel, ppmw	100. max[2]
Flash point, ° F	100. min
Gross heat of combustion, Btu/gal	130,000. min

[1] If burner includes emission controls, the limit is 5,000 ppm.

[2] If burner includes emission controls, the limit is 500 ppm.

Although it is widely known that many techniques exist for the removal of specific contaminants from used lubricating oil, there is justified concern among agencies responsible for the enforcement of environmental regulations regarding the economics of a complete process which could produce a fuel product complying with specifications such as those in table 2. Economics is very important because of market competition between recycled and virgin fuel oils. The recent soft market for fuel oils has resulted in lower prices and keener competition among fuel dealers.

REPROCESSING TO GENERATE CLEAN FUEL

Based upon available data, we recently completed a detailed performance, economic, and environmental impact analysis of processes for generating clean fuels from used oil (2).

The primary treatment technologies were categorized as 1) chemical methods, 2) solvent refining, 3) physical separation techniques, and 4) techniques to permit burning of "repackaged" but untreated waste oil.

Within each of these categories there were many options to consider. Based upon available and substantiated data, personal contacts with experts in the industry, the expertise of our own processing staff, and our broad background of used lubricating oil research, the list of processes and/or unit operations that could be evaluated from available data was narrowed to five.

It is obvious from these studies that there is no single unit operation that will demetallize, remove chlorinated solvents, and remove PCB's from waste oil in a single step, and at the same time be environmentally and economically feasible. There are several unit operations that will demetallize and remove chlorinated solvents, but hydrotreating is the only unit operation that has been shown to destroy PCB contamination in waste oil without incineration of the whole fuel.

Therefore, in order to provide practical and usable guidance in this research, it was necessary to make the presumption that all deliveries of waste oil will be analyzed for PCB contamination, and those deliveries that exceed the specified fuel standard of 5 ppmw will be rejected for use as fuel. Rejection implies returning to the generator for suitable disposition. Without this assumption, it is necessary to incorporate hydrotreating into every operation that proposes to produce fuel from waste oil. If hydrotreating becomes a part of the process, it might be an economic advantage to produce lubricating oil base stock rather than fuel oil from waste oil.

The unit operations and combinations of unit operations that were selected as a result of our literature survey and personal contacts were 1) chemical treatment with an aqueous anion solution at elevated temperatures; 2) two-stages of flash distillation; 3) flash distillation followed by thin-film evaporator; 4) flash distillation followed by solvent refining; and 5) blending (dilution) with virgin fuel oil to meet fuel standards.

Each of these unit operations was evaluated according to technical performance, economics and environmental impact.

The conclusions that were reached from these evaluations are addressed in the following discrete sections.

Chemical treatment

Chemical treatment with aqueous ammonium phosphate removes most of the metals at relatively mild conditions and in an unsophisticated and simple apparatus. The technique does not require prior removal of water or volatile components since these are removed and recovered during the heating cycle of the chemical treatment. Filtered residues are reportedly environmentally acceptable as landfill. The Phillips Petroleum Company PROP process is the primary example of this technology that has been demonstrated to be technically sound on a commercial scale (3). Filtration to remove precipitated metal salts is neither complex nor costly.

This unit operation has a moderate initial capital investment and low total fixed costs. However, it must be reiterated that using this mode of operation may be subject to patent infringement unless suitable arrangements are previously made with patent holders. It is reported that the PROP demetallization process can be licensed for a fee of $1 million. Although this may appear at first to be a large expenditure, it would probably raise the fixed costs of producing fuel from waste oil by only two cents per gallon. Licensing fees for similar procedures such as those patented by C. B. Johnson of Turbo Resources (4) are unknown, and direct negotiation between entrepreneur and the patent holder is suggested.

Variable costs for chemical treatment are lower than other options with the exception of burning by dilution. Based upon a 10 million gallon per year operation and a selling price of 53 cents per gallon for No. 2 fuel derived from waste oil, the profit would be about $0.40 per gallon, and plant payout time would be about 1-1.5 years of full production operation.

Flash distillation

Distillation using flash evaporators offers a simple system without need for chemicals or adsorbents. The distillation bottoms would contain the toxic metals in the residue. However, to separate chlorinated solvents from fuel, it is necessary to have two units in series operating at different conditions of temperature and pressure. Disposition of toxic distillation residues is also a problem, as was discussed in the section on environmental analysis. The residual distillation bottoms are not universally suitable as fuel because of their heavy metal content. They are amenable to compounding with asphaltic products, and such markets are available. Otherwise, distillation bottoms must be disposed as a hazardous waste through a licensed handler of that type of material.

Flash distillations are not an efficient mechanism for separating similar boiling range components. Therefore, it could be assumed that fuel oil would be lost to low boiling material derived from the first stage distillation and conversely, that some of the chlorinated solvents would be carried over into the fuel. Because of the relatively long contact time at high temperatures in the second stage distillation, coking will become a corrosion problem. To minimize this, the temperature and pressure must be lowered as much as possible and loss of fuel to the residue must be acceptable.

This option has favorable economics that appear comparable to chemical treatment and second only to the blending option from a dollar per gallon profit standpoint. Plant payout time is less than one year of full production operation.

Thin-film evaporator

Thin-film evaporator technology represents a unit operation totally capable of removing the bulk of metallic components from waste oil resulting in maximum recovery of the fuel component (5). The residue can be incorporated into asphaltic products without environmental endangerment, and these markets are available. A preliminary flash distillation would separate the light components containing the major portion of chlorinated solvents. This light fraction is traditionally burned as a fuel with the production of hydrochloric acid. Such an operation is permissible only if the stack gases were scrubbed to remove acidic components prior to venting to the atmosphere.

While this unit operation is a viable tool for the production of complying fuel from waste oil, it is cost-intensive as compared to most other options. The complexity of operating a thin-film evaporator would require better-trained personnel than some of the other unit operations.

The economics of thin-film evaporation are aided somewhat by the relatively high yields of product compared to the two-stage flash distillation option, but some of this advantage may be lost in byproduct credits.

Solvent refining

The solvent extraction step selected from a re-refining process (6-7) has been demonstrated to remove over 95 percent of the lead from waste oil. At today's typical lead levels, this should be adequate to reduce the lead to meet any fuel standards.

The process requires a preliminary flash distillation to remove light components and chlorinated solvents.

The process economics are not favorable as compared to some other unit operations because of the solvent recovery requirements. The process is also labor-intensive because of the additional unit operations involved.

An economic evaluation showed this option to have the second highest initial capital investment and the lowest rate of return of any that were studied. Even so, the payout period is calculated at 2-3 years.

Blending

Although this single unit operation has been shown to be the most attractive from a technical viewpoint; it fell to third economically and to last from an environmental evaluation. While dilution would make it appear that lead, arsenic, chromium, cadmium, PCB's and hydrochloric acid emissions were controlled, no change in the quantities released to the environment has been accomplished. This unit operation has the third highest capital investment requirement ($4.81 million), the lowest fixed costs, 0.10 cents per gallon; the lowest variable costs, $0.02 per gallon; and the highest profitability, $0.43-0.44 per gallon. However, it was third in payout time, 1.5-2 years.

TABLE 3. - Summary of costs for selected waste oil recycling processes (1987$)

	Process				
	Chemical treatment	Flash distillation	Flash dist/ thin-film evap.	Flash dist/ solvent refining	Blending
Cap. Inv. (CI)					
MM $	$4.455	$4.076	$6.528	$5.338	$4.806
Operating costs, $/gal					
Fixed costs					
10-yr amortization	$0.10	$0.12	$0.15	$0.13	$0.08
15-yr amortization	$0.08	$0.09	$0.12	$0.10	$0.07
Variable costs, $/gal					
Best case	$0.04	$0.03	$0.08	$0.21	$0.02
Worst case	$0.04	$0.10	$0.14	$0.27	$0.02
Fixed plus variable Costs, $/gal					
Best case	$0.14	$0.15	$0.23	$0.34	$0.10
Worst case	$0.12	$0.19	$0.26	$0.37	$0.09
Product value, $/gal					
As No. 2 fuel oil	$0.53	$0.53	$0.53	$0.53	$0.53
As No. 6 fuel oil	$0.41	$0.41	$0.41	$0.41	$0.41
Estimated process yield, %	75	60	75	70	98
Profit, $/gal					
Selling as No. 2 oil					
Best case	0.39	0.38	0.30	0.19	0.43
Worst case	0.41	0.34	0.27	0.16	0.44
Selling as No. 6 oil					
Best case	0.27	0.26	0.18	0.07	0.31
Worst case	0.29	0.22	0.15	0.04	0.32
Plant payout, years					
Best case	1.08	0.78	1.73	1.85	1.47
Worst case	1.32	0.95	2.11	2.26	1.79

ENVIRONMENTAL CONSIDERATIONS

It is noteworthy that the industry standard of past decades, the acid/clay process, has not been included in the above discussion. While there are still some plants around the world using this technology, they are becoming rare as the pressures to clean up the ecosystem grow. The various gaseous, liquid, and solid by-products from this process do not seem amenable to economical treatment. The next environmental issue may be the use of clay. As can be seen from the preceding discussion, clay is used extensively as the finishing or polishing step in re-refining, and in one case the entire process depends on a severe clay treatment. While clay almost always produces a high quality product, it does not always remove the hazardous contaminants that are increasingly being mixed with used oil either by generators or collectors. For example, it can be shown that polychlorobiphenyls (PCB's) are essentially unaffected by clay contacting and come through with the lube oil fraction in most processes. Thus, the product could end up being a hazardous waste, which would seriously impair handling and marketing. Those processes incorporating hydrotreating seem to have solved this potential problem. Most hazardous materials reportedly are converted to relatively innocuous species during this reaction (8). Claims have been made that the relative costs of hydrotreating and clay contacting are comparable (9). Adding in escalating environmental permitting and hazardous waste disposal costs can tip the balance toward hydrotreating.

A major problem plaguing used oil recycling is contamination of the oil during collection. A growing number of studies show increasing types and quantities of hazardous wastes mixed into the oil (10,11). This has forced Congress and the U.S. Environmental Protection Agency to propose declaring used oil a hazardous waste (2). Regulations are already in place to restrict those used oils that can be burned as fuel in nonindustrial boilers (3).

The proposed used oil management plan (2) should help re-refining, since the incoming oil will have to be analyzed in some detail. This may add several cents per gallon to the processing costs. Since re-refiners tend to perform much of this testing anyway, it should make them more competitive with those who in the past sold the used oil as fuel with little or no testing or treatment.

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